EFFECT OF MULTI-WALL CARBON NANOTUBES ON THE PERFORMANCE OF SELF-HEALING RUBBER

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EFFECT OF MULTI-WALL CARBON NANOTUBES ON THE PERFORMANCE OF SELF-HEALING RUBBER

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled ‘The effect of multi-wall carbon nanotubes on the performance of self-healing 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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Date:

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LIST OF SYMBOLS

%	Percentages
phr	Part per hundred rubber
˚C	Degree Celsius
wt%	Weight percent
kJ/m^2	Joule per square meter
MJ/m^3	Joule per cubic meter
g/cm^3	Gram per cubic centrimeter
g/mL	Gram per mililitre
g	Gram
Psi	Pound per square inch
mm	Milimeter
mm/min	Milimeter per minute
N/mm	Newton per milimeter
σ	Tensile strength
Φ_r	Volume fraction of swollen rubber
V_0	Molar volume
ρ	Density
m	Meter
mol/cm^3	Molar concentration per cubic centimeter
cm^{-1}	Number of wavelength per centimeter
G’	Storage modulus
G’’	Loss modulus
Hz	Hertz
˚C/min	Degree Celsius per minute

η*	Complex viscosity
mV	Milivolt
nm	Nanometer

LIST OF ABBREVIATIONS

AA	Acrylic Acid
AC	Alternating Current
BIIR	Bromobutyl Rubber
BR	Butadiene Rubber
CB	Carbon Black
CNT	Carbon Nanotube
CVD	Chemical Vapourization Deposition
DA	Diels-Alder
DC	Direct Current
DCP	Dicumyl Peroxide
DMF	N, N-dimethylformamide
DSC	Differential Scanning Microscopy
ENR	Epoxidized Natural Rubber
EPM	Ethylene-Propylene Rubber
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
IL	Ionic Liquid
IPDI	Isophorone Diisocyanate
LVE	Linear Viscoelastic
MWCNT	Multi-wall Carbon Nanotube
NMP	N-methyl-2-pyrrolidone
NR	Natural Rubber
NT	Nanotube
PB	Polybutadiene

PCL	Polycaprolactone
PDM	Pyridinedimethanol
PMMA	Poly (methyl methacrylate)
PP	Polypropylene
PS	Polystyrene
PTMEG	Polytetramethylene ether glycol
PZT	Polymerized Zinc Thiolate
SDDBS	Sodium Dodecyl Benzene Sulfonate
SEM	Scanning Electron Microscopy
SWCNT	Single-wall Carbon Nanotube
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
XNBR	Carboxylated Nitrile Butadiene Rubber
XRD	X-ray Diffraction
XSBR	Carboxylated Styrene Butadiene Rubber
ZDEC	Zinc Thiolate
ZDMA	Zinc Dimethacrylate
ZnO	Zinc Oxide

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ABSTRAK

Untuk memenuhi keperluan produck akhir, getah perlu dirangkai silang untuk membentuk rangkaian kovalen 3D. Walau bagaimanapun, proses pemvulkanan menjadikan getah bertindak seperti thermoset dengan kemustahilan untuk sembuh sendiri. Dari sudut pandangan pembangunan mampan getah, ia adalah penting untuk mengintegrasikan keupayaan penyembuhan diri ke dalam getah komersial. Prestasi mekanikal getah penyembuhan sendiri perlu dipertingkatkan melalui penambahan pengisi untuk memenuhi permintaan. Kajian ini bertujuan untuk menilai dan menyiasat kesan tiub nano karbon berbilang dinding terhadap sifat sebatian getah penyembuhan sendiri. Dalam kerja ini, jumlah tiub nano karbon berbilang dinding yang berbeza telah ditambah ke dalam getah asli penyembuhan sendiri untuk menilai kesan tiub nano karbon berbilang dinding kepada keupayaan penyembuhan dan prestasi mekanikal. Didapati bahawa kekuatan tegangan dan kekuatan koyak meningkat dengan kandungan tiub nano karbon berbilang dinding. Penambahan tiub nano karbon berbilang dinding meningkatkan ketumpatan pautan silang sebatian getah asli penyembuhan sendiri. Kekasaran di Kawasan patah telah meningkat seperti yang diperhatikan mengguna mikroskop elektron pengimbasan. Daripada imej mikroskop elektron pengimbasan, jurang kecil diperhatikan pada garis potong untuk getah asli dengan 6 phr tiub nano karbon berbilang dinding mungkin disebabkan oleh penamahan tuib nano karbon berbilang dinding mengurangkan tindak balas antara radikal PZT dengan zink tiolat dan molekul getah sebagai kandungan tiub nano karbon berbilang dinding meningkat. Keputusan juga mendedahkan bahawa getah asli penyembuhan sendiri dengan 6 phr tiub nano karbon berbilang dinding mempunyai modulus storan tertinggi. Penambahan tiub nano karbon berbilang dinding juga meningkatkan kesan payne kompaun getah. Kekonduksian sebatian getah asli penyembuhan sendiri meningkat dengan kandungan tiub nano karbon berbilang dinding. Keputusan DSC menunjukkan bahawa suhu peralihan kaca kekal tidak berubah dalam kehadiran tiub nano karbon berbilang dinding yang dipercayai bahawa kehadiran pengisi tidak mempunyai kesan ke atas suhu peralihan kaca.

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ABSTRACT

In order to meet the requirement of final product, natural rubber need to be crosslinked to form 3D covalent network. However, the vulcanization process turns the gum rubber to act like thermoset with the impossibility to self-heal. From the view point of sustainable development of rubbers, it is substantial to integrate the self-healing capability into commercial rubber. The mechanical performance of self-healing rubber need to be enhanced through addition of filler in order to fulfil the demand. This study aimed to assess and investigate the effect of multi-wall carbon nanotubes on the properties of self-healing rubber compound. In this work, different amount of multi-wall carbon nanotube was added into the self-healing NR in order to assess the effect of multi-wall carbon nanotube on the heal ability and mechanical performance. It was found that the tensile strength and tear strength increased with the multi-wall carbon nanotube content. The addition of multi-wall carbon nanotube increased the crosslink density of the self-healing NR compound. The roughness at the fracture area was increased as observed using scanning electron microscope. From SEM images, a small gap was observed at the cut line for NR with 6 phr of multi-wall carbon nanotube which may be due to the addition of multi-wall carbon nanotube reduced the reaction between PZT radical with zinc thiolate and rubber molecules as the multi-wall carbon nanotube content increased. The results also revealed that the self-healing NR with 6 phr of multi-wall carbon nanotube have the highest storage modulus. Addition of MWCNT also increased the payne effect of the NR compound. The conductivity of self-healing NR compound increased with the content of multi-

wall carbon nanotube. The results of DSC showed that the glass transition temperature stay unaltered within the presence of multi-wall carbon nanotube which was believed that the presence of filler has no effect on the glass transition temperature.

CHAPTER 1

INTRODUCTION

1.1 Background to the Research

The ability of self-healing materials to fix themselves spontaneously after mechanical damage is drawing more attention. These polymers are able to restore their original structures and functionalities after being damaged. Some of these materials are easy to produce, exhibit consistent self-healing, and have outstanding mechanical qualities (Cordier et. al, 2008). The molecular chain mobility must be sufficient to achieve molecular interdiffusion and rearrangement in order to introduce self-healing capabilities. In order to achieve the self-healing recovery, a reversible bond with a high enough amount of chain mobility can be inserted (Lee, 1995).

For most self-healing materials, healing requires external stimuli. For instance, a polymer that can repair when heated has non-covalent supramolecular connections added to it (Wietor et al., 2008). However, it would be ideal if the rubber could repair on its own without any external stimuli. A dynamic supramolecular method was created by Cordier et al. to create a self-healing rubber containing multivalent hydrogen bonds. At room temperature, they can come together to create a network despite their individual fragility. This network enables damage to be repaired. Contrary to typical cross-linked or thermo-reversible rubbers formed of macromolecules, these systems are capable of self-healing when cut or broken by bringing the fractured surfaces together. Healing is a cyclical process. According to Chen et al. (2002), these supramolecular elastomers don't require the inclusion of any more energy (like heat or light), healing substances (such monomers and catalysts), plasticizers, solvents, or plasticizer precursors. When the broken crosslinks come into contact with the cut surfaces, they reform and the polymer chains begin to self-diffuse. Because of this, the two separated portions can rejoin even at room temperature.

Natural rubber (NR), which is made from the sap (latex) of the rubber-producing plant Hevea brasiliensis, is one of nature's amazing materials. It is well-liked since it is made of long cis-1,4-polyisoprene and has better qualities than other synthetic rubbers. To accomplish the goals of sustainable development, the rubber industry must, nevertheless, overcome some formidable obstacles (Tanasi et. al, 2019).

With the synthesis of both long chains and cross-links across the chains, supramolecular rubber exhibits self-healing behaviour, enabling recoverable extensions of up to several hundred percent in the creation of rubber materials with self-healing behaviour. The rubber industries demand materials with a long shelf life and exceptional mechanical properties in a variety of climatic situations.

Although the elastomer had outstanding self-healing capabilities, its mechanical properties made it unsuitable for industrial use. The incorporation of filler into the elastomer is a frequent strategy to improve mechanical performance. Self-healing effectiveness may be improved by adding nanofillers like graphene and carbon nanotubes (CNT) to the matrix (Wang et al., 2020). The balance between the mechanical properties and the self-healing performance must be maintained while creating a self-healing rubber. It becomes difficult since the mechanical characteristics are affected by a hard and stable covalent crosslinked network while the self-healing behaviour depends on a flexible dynamic reversible crosslinked network (Bai et al., 2015).

The most widely utilised of all the reinforcing fillers used in the rubber industry to increase the performance of the elastomers is carbon black, which improves the product's qualities to meet the demands of varied applications. The traditional vulcanizate NR frequently has filler that contains carbon black. Due to its superior mechanical characteristics, this compounding technology is frequently utilised, particularly in the production of tyre threads. The impact of carbon black filler on the ability of rubber to self-heal, however, has not received enough research.

Due to their nanoscale carbon fibres, carbon nanotubes (CNTs) have sparked intense interest in both research and applications. Graphite sheets that have been coiled up into cylindrical shapes with a diameter of roughly 100nm are what CNTs are known as. CNTs have outstanding mechanical qualities, thermal stability, and electrical conductivity thanks to their unique molecular structure. Additionally, CNTs' high aspect ratio and vast surface area make it easier for them to interact with the molecules of rubber. The quantity of carbon layers in a carbon nanotube determines its class. Single-walled carbon nanotubes are single graphene layers with diameters between 0.4 and 2 nm (SWCNTs). It typically manifests as bundles that are hexagonally packed. The diameter of multi-walled carbon nanotubes (MWCNTs), which have two or more cylinders, varies between 1 and 3 nm (He et al., 2013). The composites' ability to conduct electricity may contribute to the creation of heat within the rubber matrix, which could enhance rubber's ability to heal itself.

1.2 Problem Statement

Elastomers are now often employed in many different applications, including tyres, conveyor belts, and seals. The development of deformation-induced damage is cumulative for typical elastomers. Once the damage has formed, it cannot be repaired afterwards. Self-healing materials are designed to repair any local damage with an external trigger, improving a structure's long-term endurance. Conventional vulcanised rubbers lack this potential since their stable covalently bonded threedimensional molecular network provided them with good and consistent mechanical performance. Therefore, creating self-healing elastomer is difficult. Self-healing NR with MWCNT as reinforcing nanofillers is investigated in this work.

Because of the strong hydrogen bonds formed by the polar functional groups on the surfaces of CNTs and the Van der Waals interactions between the CNT particles and these groups, CNTs have a high propensity to aggregate, which results in composites with a variety of characteristics when CNTs are added to an NR matrix. The mechanical performance of the elastomers as well as the reinforcing effects of CNTs may be diminished by their poor dispersion in the rubber matrix. In order to reduce the formation of agglomerates, MWCNTs are compounded into the self-healing rubber in this study using melt blending. The effect of MWCNTs on the performance of self-healing natural rubber is studied.

1.3 Objectives

This research examines the impact of multi-wall carbon nanotubes on the performance of self-healing rubber. Natural rubber (NR) is used as the raw rubber. The research objectives are as follows:

i. To fabricate and characterize the self-healing rubber compound

ii. To assess and investigate the effect of multi-wall carbon nanotubes on the properties of self-healing rubber compound

1.4 Thesis Outline

Chapter 1: Includes background of the research, problem statement and objectives

Chapter 2: Consists of literature review of the research, extensive for self-healing rubber, and carbon nanotubes

Chapter 3: Describe the raw materials used in this study, experimental procedures used, and machine that used to generate the research’s experimental data

Chapter 4: In-depth information on the morphological and mechanical properties of MWCNT reinforced self-healing rubber will be presented, along with data and results that were acquired.

Chapter 5: Conclusion on this present work and the suggestion for the further study

Chapter 6: List of references used in this study

CHAPTER 2

LITERATURE REVIEW

2.1 Self-healing rubber

One of the resurgences of intelligent materials in engineering materials that may recover itself and compatibility when degraded without the need for any manual assistance is self-healing rubber, also known as self-recovering rubber. This idea was put up in the 1980s to repair invisible microcracks and increase safety by prolonging the useful life of the materials. Strong self-healing elastomers are anticipated to have good mechanical properties and the capacity for repeated healing (Lai et al., 2018).

According to Li et al. (2019), natural rubber (NR), which does not fit into any useful practical categories, is one of the causes of the lack of self-healing shown in tests employing raw rubber. Consequently, it is difficult to find rubber-based polymers that can self-heal at room temperature. By incorporating an ionic supramolecular network with NR, Xu et al. (2016) developed a useful strategy. The research did not provide concrete evidence that the ionic supramolecular network was successfully grafted onto the NR molecular chains, though. There hasn't been much investigation into whether NR can be produced as self-healing rubber.

Rubbers are widely used in many industries, especially the automotive sector (Sienkiewicz et al., 2017). Recently, new techniques have been developed for the reversible non-covalent and covalent cross-linking used in the production of eco-friendly rubber. Rubbers created by reversible non-covalent cross-linking feature weak hydrogen bonds, poor ionic strength, and poor crystallinity because of the weak interactions (Okada et al., 2001).

Self-healing rubber is often manufactured using either extrinsic methods or intrinsic methods. A healing agent is enclosed and implanted in a rubber matrix in an extrinsic system. The healing agent is released when the material breaks, covers the damaged area, and repairs its functionality. The nonrecurring action of this extrinsic self-healing system, which can only repair the damage at the specified place once, makes it contraindicated. Additionally, the capsule usually disintegrates as a result of the high shear forces required for rubber processing during mixing and compounding (Blaiszik et.al., 2010). The intrinsic technique, on the other hand, uses intricate, reversible chemical linkages inside the material to enable multiple healing at the same site. Diels-Alder reaction, radial-based system, hydrogen or halogen supramolecular contacts, as well as ionic interactions, can all be used to start reversible chemical bonds (Zechel et. al., 2017).

2.1.1 Diels-Alder (DA) reaction

Use of strong covalent cross-linked rubber, which can give rubbers more mechanical strength, is hence more advantageous. Systematically examined reversible covalent cross-linkers included imine bonds, boronic esters, and disulfide. The thermo-reversible Diels-Alder (DA) reaction was the technique most frequently employed to create reversible infrastructure in rubbers.

One method for achieving reversible crosslinking is the use of Diels-Alder (DA) reactions. An electron-rich diene and an electron-poor dienophile undergo a [4+2] cycloaddition process to form a cyclohexene adduct that can undergo a retro-DA reaction (rDA) at a high temperature. Furan and maleimide group reactions are one instance of a DA reaction.

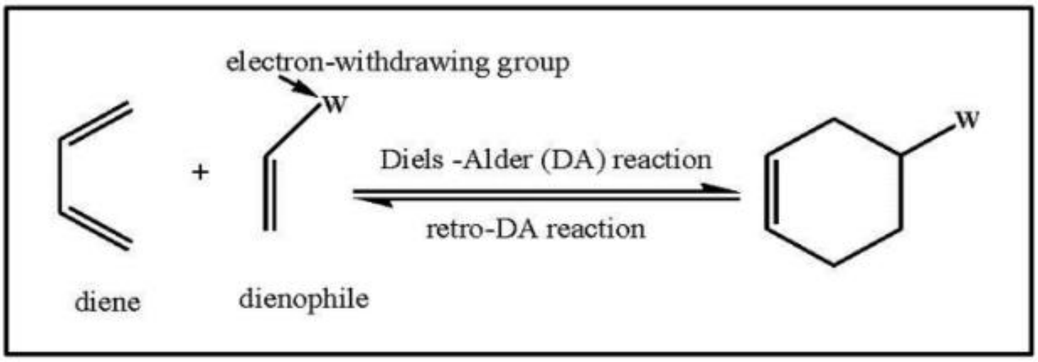

Figure 2.1: Schematic representation of thermally reversible Diels-Alder (DA) reaction of diene with dienophile (Tasdelen, 2011)

While Polgar et al. (2015) experimented with ethylene-propylene rubber, Trovatti et al. (2015) investigated the thermo-reversible DA method for recycling BR that had been furan- and bismaleimide-modified. The first thermoreversible DA reaction-based self-healing polymer has been disclosed by the Wudl group. Without materially altering the current characteristics, the DA moieties enable self-healing in the polymer networks. (Liu & Chuo, 2013). Tasdelen (2011) claimed that because of the DA reaction's remarkable adaptability, effectiveness, and selectivity, it is referred to as a "click" reaction. It also happens quickly with reasonably fast kinetics under relaxed reaction conditions to provide a high yield. Because of the DA mechanism uses an addition reaction rather than a condensation process, there are no by-products produced. In addition, it can happen in the absence of a catalyst. (Imbernon et al., 2015).

2.1.2 Disulphide metathesis

Disulphide groups have the potential to be used to give self-healing properties to elastomeric materials because of the substantial function that sulphur plays as a crosslinking agent in the rubber vulcanization process (Hernández et al., 2016). Dynamic covalent bond formation is frequently used as a substitute for DA chemistry because the latter requires relatively high temperatures that may not always be accessible in service applications. Disulphide exchange or a thiol-disulphide exchange reaction can be used to dynamically rearrange disulphide groups. These exchange processes frequently take place in response to environmental elements like heat, light, and pH. Figure 2.2 shows the general reaction of the disulphide interchange process (Canadell et al., 2011). A self-healing elastomer that can perform disulphide exchange at ambient temperature has also been developed by researchers.

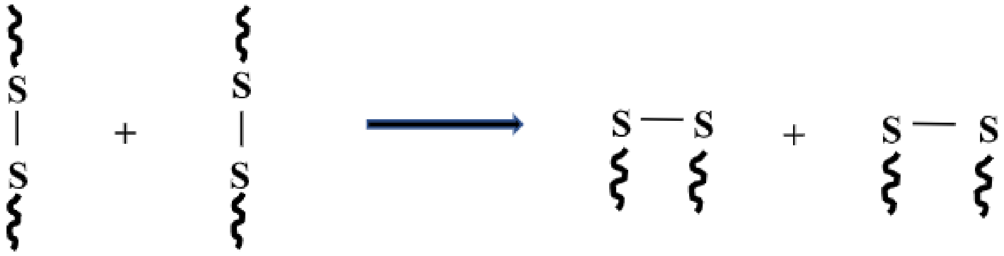

Figure 2.2: Disulphide interchange reaction (Canadell et al., 2011)

2.1.3 Supramolecular interaction

a) Hydrogen bonding

Hydrogen bonding shown the weakest binding strength of any supramolecular interaction type, but it is nonetheless frequently utilised to create dynamic, reversible elastomers with self-healing capabilities. Leong and Butler changed butadiene rubber derivatives by reacting them with triazoline diones, resulting in the development of hydrogen bonds between two urazole groups, and created the first supramolecular elastomer through these linkages. The substance, however, behaved like a thermoplastic elastomer, rendering commercial rubber applications inappropriate for its use.

Using the similar methodology, self-healing polybutadiene rubber (PB) was developed by Wang et al. (2015), however their study was remarkable because it incorporated proton transfers between organic cations and anions as well as ionic hydrogen bonding. These ionic hydrogen bonds demonstrated exceptional stability and simple accessibility and are typically created in an acid-base reaction. Figure 2.3 (a) illustrates how two oligomers were created in this study by combining PB with amine and carboxylic acid via a thiol-ene reaction. Eventually, during the mixing procedure, the oligomers were put together to create ionic hydrogen bonds via a proton transfer reaction between the carboxylic acid and amine groups. In addition, the supramolecular PB was exposed to UV light to create a covalent crosslinked network, as seen in Figure 2.3 (b). The elastomer was able to self-heal thanks to the dynamic reversible ionic hydrogen bonding, with tensile strength recovering up to 90% after 12 hours of the healing process at ambient temperature. With a stress at break of just 1.78 ± 0.18 MPa, the supramolecular elastomer, however, has rather poor tensile characteristics and would not be able to withstand heavy loads in engineering applications.

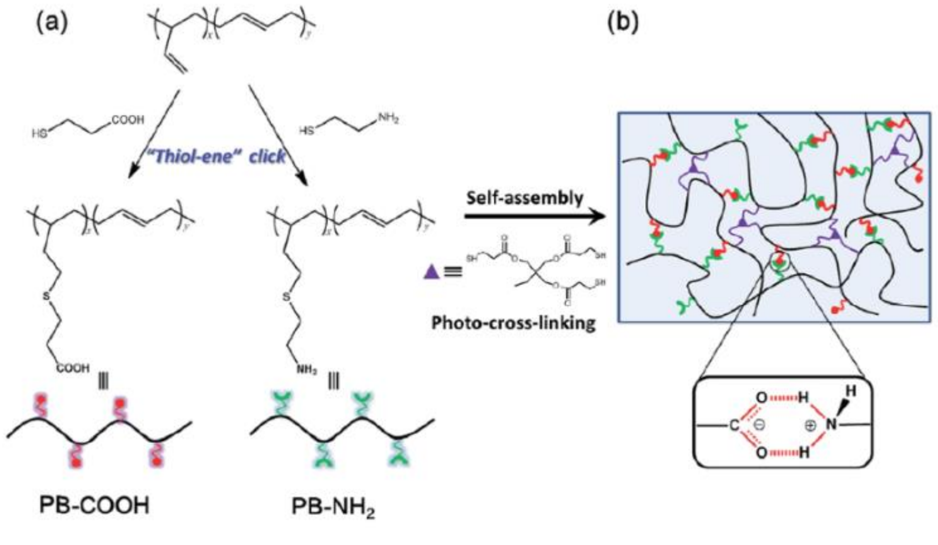

Figure 2.3 (a) Thiol-ene reaction of PB with amine and carboxylyic acid (b) Supramolecular PB network with ionic hydrogen bonds and covalent crosslink (Wang et al., 2015)

Li et al. (2021) created a self-healing, high-performance polyurethane elastomer at ambient temperature. Tensile strength was measured at 29.0 MPa, which is a remarkable result. Fracture energy was measured at 121.8 MJ/m^3 and 104.1 kJ/m^2.

By synthesising polytetramethylene ether glycol (PTMEG), isophorone diisocyanate (IPDI), and 2,6-pyridinedimethanol (PDM), which enabled it to generate extra hierarchical H-bonding, it was possible to produce linear polyurethane with two different kinds of building blocks. The hydrogen bonding produced by the urethane bond was also used by Chen et al. (2012) as the self-healing process for polyurethane in addition to the van der Waals interaction. At 25 ◦C, 50 ◦C and 75 ◦C, the healing process was carried out. At 50 ◦C, the maximum rate of recovery, roughly 67% was attained. The tensile strength value below 1 MPa was, nevertheless, regarded as low.

By grafting acrylic acid (AA) with a content ranging from 2 to 4 phr into a polycaprolactone/natural rubber (PCL/NR) blend, hydrogen interactions were also introduced (Lai et al., 2020). The healing efficiency gradually increased, reaching its highest percentage at 62.8 % when the material was healed at 60 °C and 80 °C, according to the data, which generally showed that adding more AA somewhat affected the self-healing elastomers' strength (Figure 2.4 & Figure 2.5). These show the hypothesis of the self-healing idea that mechanical performance and self-healing efficacy are incompatible. For NR/PCL-g-AA (60/40), 2-phr of AA is the ideal amount to provide the best healing efficiency because the efficiency value falls off at 4-phr of AA. Even yet, the trend will be easier to forecast if the AA content varies more. The pure PCL and NR mixture has a restricted capacity for self-healing of less than 50% in the absence of hydrogen interactions.

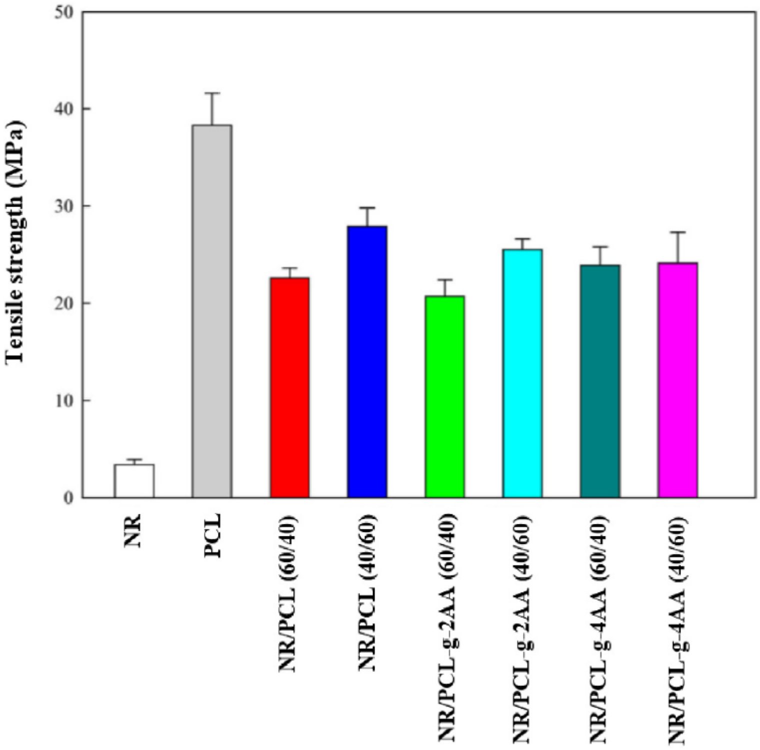

Figure 2.4: Tensile strength of NR, and PCL, and the NR/PCL and NR/PCL-g-AA blends (Lai et al., 2020)

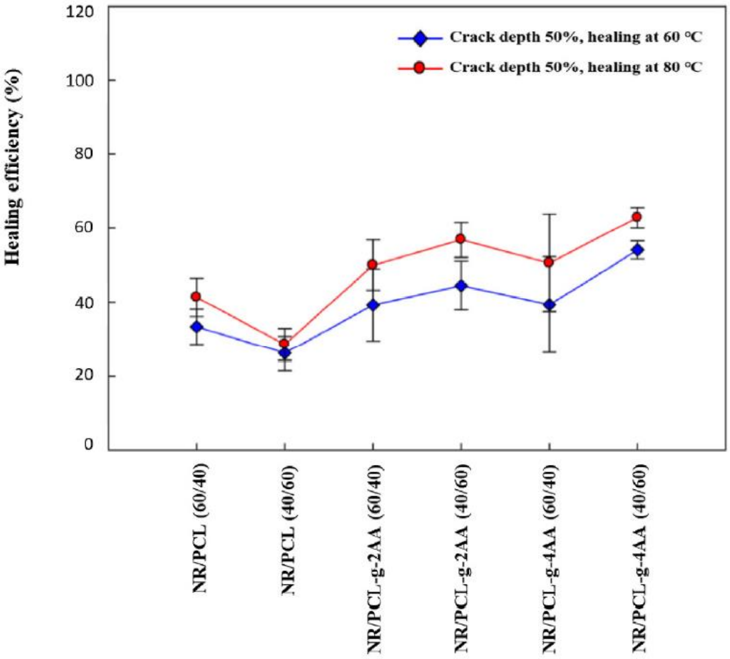

Figure 2.5: Healing efficiency of NR/PCL, NR/PCL-g-2AA, and NR/PCL-g-4AA blends (Lai et al., 2020)

b) Ionic bonding

Ionic bonding is a different strategy for self-healing rubber (Miwa et al., 2018). This idea creates rubber chain polymerization growth without a termination phase, allowing the natural rubber chain to regenerate after being cut (Zhang et al., 2019). According to Das et al. (2008), by converting the bromine functionalities of bromobutyl rubber (BIIR) into ionic imidazolium bromide groups, bromobutyl rubber (BIIR) can be made to be self-healing. Due to the reversibility of the ionic connections, a cut sample might regain its original characteristics. The non-polarity of the majority of commercial rubbers, however, limits the ability to form ionic connections on rubber chains. As a result, there are no functional groups that can be changed into ionic groups. The creation of rubber with ionic connections seems to be a suitable solution for adding self-healing properties.

Xu et al. (2016) studied the construction of self-healing supramolecular rubbers by adding ionic cross-links to natural rubber by controlled vulcanization. A self-healing rubber was created using zinc dimethacrylate (ZDMA) without the need for laborious molecular structure modifications. A Zn^{2+} is often an ionic chemical that reacts easily with rubber molecules. ZDMA can easily be grafted-polymerized onto rubber chains during peroxide-induced vulcanization, according to Xu et al. The natural rubber exhibited an exceptional self-healing behaviour thanks to the ionic supramolecular network.

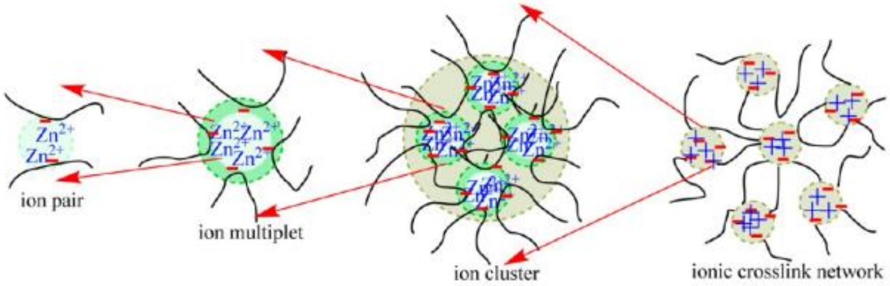

Figure 2.6: Schematic illustrations of Zn^{2+} induced ion pair, ion multiplet, ion cluster, and the final ionic cross-link network (Xu et al., 2016)

The ions integrated into a non-polar molecule either induce a dipolar character or interact with a polar molecule to generate dynamic, reversible ionic connections. Due to the electrostatic interaction, these reversible ionic connections prefer to form ionic clusters (Yang & Urban, 2018). Strong bond association force produced by the aggregation of ion clusters leads to a more stable supramolecular connection (Peng et al., 2018). Additionally, the ion clusters function as reinforcing elements that limit chain mobility and improve the performance of the material (Nie et al., 2010). In this study, self-healing behaviour was added to natural rubber by using zinc thiolate as an ionic cross-linker. Natural rubber's self-healing capacity is activated at room temperature without the need for outside assistance when zinc thiolate is incorporated.

The potential reaction mechanisms between zinc thiolate and natural rubber in the presence of DCP to produce reversible metallic ion networks for self-healing is as shown in Figure 2.7. Homolytic breakdown of peroxides into free radicals is the first step in the mechanism. In order to create crosslink precursors, the peroxide free radical species may interact with rubber chains or zinc thiolate. These reactions help crosslinks to form. The primary interaction between peroxide free radical species and rubber chains involves radical species that are highly reactive and unstable abstracting allylic hydrogens from the rubber chains and then recombining to form crosslink. Due to the existence of steric hindrance in the double bonds and the quantum of allylic Hatoms, the reaction of peroxide free radical species with the double bond of rubber chains is less pronounced (Kruzelak et al., 2017).

The self-healing network is created by the vulcanised zinc thiolate on the rubber chains, which is composed of Zn^{2+} and two S^{-}. Strong electrostatic interaction between neighbouring Zn^{2+} ion intermediates are brought about by interactions between ion pairs. This causes the production of ionic multiplets, which then combine to form ion clusters and limit the rubber chains' flexibility and mobility (Basu et al., 2014). Larger ion networks are formed when ionic cluster aggregate sizes increase. These reversible ionic networks serve as physical cross-linking points that trigger self-healing processes. Covalent and ionic networks are both destroyed by local damage. When two fractured surfaces come into contact, the ionic network will rearrange, allowing the cracked surface to adhere even when the covalent bonds would not be able to rebuild. As the ionic network recovers and the molecular chains rearrange, new molecular entanglement and material recovery result. Table 2.1 shows the common approaches of self-healable elastomer.

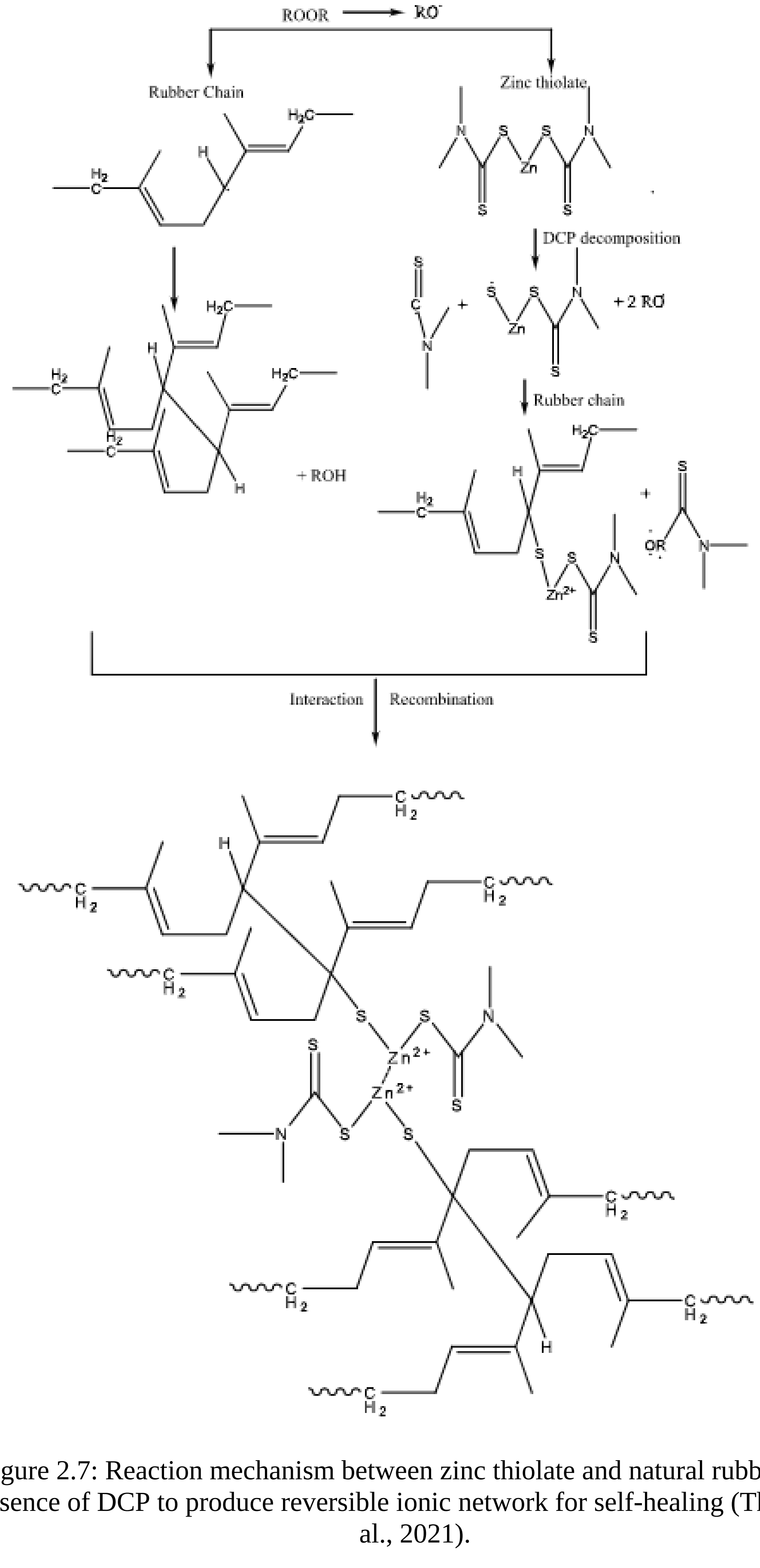

Figure 2.7: Reaction mechanism between zinc thiolate and natural rubber in the presence of DCP to produce reversible ionic network for self-healing (Thajudin et al., 2021).

Table 2.1: Common approaches of self-healable elastomer

Elastomers	Healing Approaches	References
Natural Rubber (NR)	Disulphide crosslink Hydrogen bonding Ionic bonding	(Hernández et al., 2016) (Chino and Ashiura, 2001) (Xu et. al., 2017)
Epoxidized Natural Rubber (ENR)	Disulphide crosslink Dynamic crosslink	(Imbernon et al., 2015) (Rahman et al., 2013)
Bromobutyl Rubber (BIIR)	Ionic imidazole-bromide bond	(Sallat et al., 2018)
Carboxylated Styrene Butadiene Rubber (XSBR)	Ionic bond Diels Alder	(Xu et. Al., 2016) (Kuang et al., 2016)
Butadiene rubber	Diels Alder Disulphide crosslink	(Trovatti et al., 2015) (Xiang et al., 2015)
Carboxylated Nitrile Butadiene Rubber (XNBR)	Dual Crosslink	(Lenko et al., 2013)

2.2 Carbon nanotubes

With interest in carbon nanostructures expanding quickly over the past decade or so with the discovery of buckminsterfullerene, carbon nanotubes, and carbon nanofibers, they are starting to have commercial significance. Carbon nanotubes (CNTs) have special mechanical, electrical, and magnetic properties that have drawn a lot of research attention to them. With tensile strengths greater than steel but only one-sixth the weight, CNTs are arguably the strongest materials that will ever exist. Iijima (1991) used the arc discharge technique to make the initial discovery of carbon nanotubes (CNTs). Following this finding, numerous scientific studies were started, and various techniques, including arc discharge, laser vaporisation, and catalytic chemical vapour deposition of hydrocarbons, were utilised to create CNTs (Richard, 2001; Ebbesen, 1997; Andrews et al., 1999). A structure based on a perfect arrangement of these connections aligned along the axis of nanotubes would result in an incredibly strong material because carbon-carbon covalent bonds are among the strongest found in nature. Nanotubes are robust, flexible structures that can be shaped by stretching and bending them without suffering catastrophic structural breakdown (Tanaka et al., 1999). These nanotube reinforcements would enable the production of incredibly strong and light materials, similar to the existing carbon fibre technology. Scientists from all around the world have been interested in CNTs because of their exceptional capacity to absorb loads placed on nanocomposite materials.

Since the discovery of carbon nanotubes (CNTs) in 1991, a great deal of thought has gone into the possibility of these tubular nanofillers to reinforce polymeric materials. The capacity of CNT to act as reinforcement in a variety of elastomeric matrices has been the subject of numerous investigations. To improve these matrix materials' characteristics, CNTs are frequently disseminated into metals, ceramics, and polymers, respectively (Dong et al., 2001).

These days, because to its exceptional properties, MWCNTs are widely used as an elastomer's reinforcing agent. MWCNTs have excellent application potential in a variety of sectors, including electromagnetic interference shielding, sensors, Li-ion batteries, and nanocomposites, because of their exceptional mechanical properties and strong electrical and thermal conductivities (Liu et al., 2017). The mechanical characteristics and electrical/thermal conductivities of the resultant composites can be greatly enhanced by the addition of MWCNTs to polymers (Liu et al., 2004). The dispersion of MWCNTs in the polymer matrix often plays a dominant role in maximizing the translation of MWCNTs' distinctive features to the polymer composites.

2.2.1 Synthesis of CNT

The nanotube synthesis by a CVD approach was chosen because it offers a promising route to the mass production of high purity nanotubes that may be exploited for commercialization. High purity and usable (i.e., easily dispersible) nanotubes must be available in mass for useful composite research. Existing single-wall nanotube (SWNT) synthesis methods do not provide the necessary volumes or levels of purity. The oxidative shortening process used to purify these materials is frequently time-consuming, yield-poor, and harmful to the tubes' structural integrity (Sinnott & Andrews, 2001). Multiwall nanotubes are expected to be favoured over SWNTs on a cost basis for applications like conductive fillers or as reinforcing fibres. Additionally, up to an industrial level, technologies created for MWNT applications can be easily applied to SWNT composites. A synthesis technique was created to satisfy the following requirements: bulk manufacturing, cheap cost, high purity, and properly aligned (unentangled) product (Andrews et al., 1999). The system is relatively simple, consisting of a quartz tube reactor within a multizone furnace (Figure 2.8). According to Rao et al. (1998), entraining a mixture of xylene and ferrocene into an inert gas stream is part of the system configuration. Iron nanoparticles are formed during the decomposition of the ferrocene-xylene combinations at temperatures between 625-775 °C and at atmospheric pressure, and they start to deposit well-aligned pure MWNT arrays on the quartz surfaces (reactor walls and substrates). Typical nanotube products, illustrating purity and alignment, are shown in Figure 2.9.

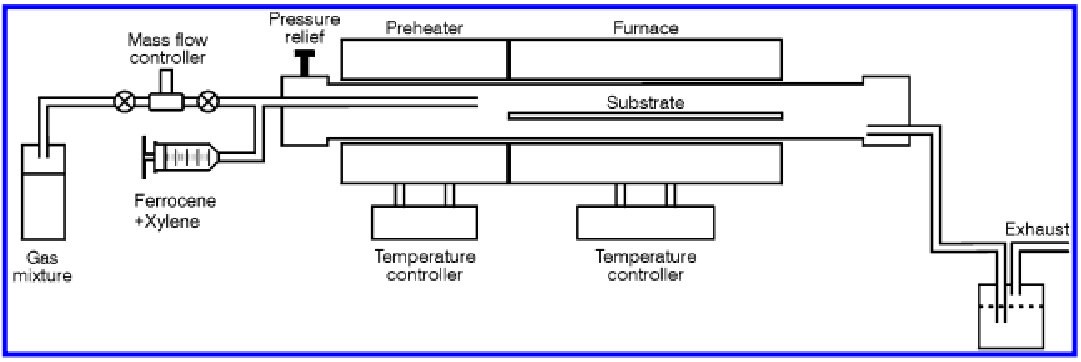

Figure 2.8: Schematic of floating catalytic CVD reactor system to produce MWCNTs (Andrews et al., 1999)

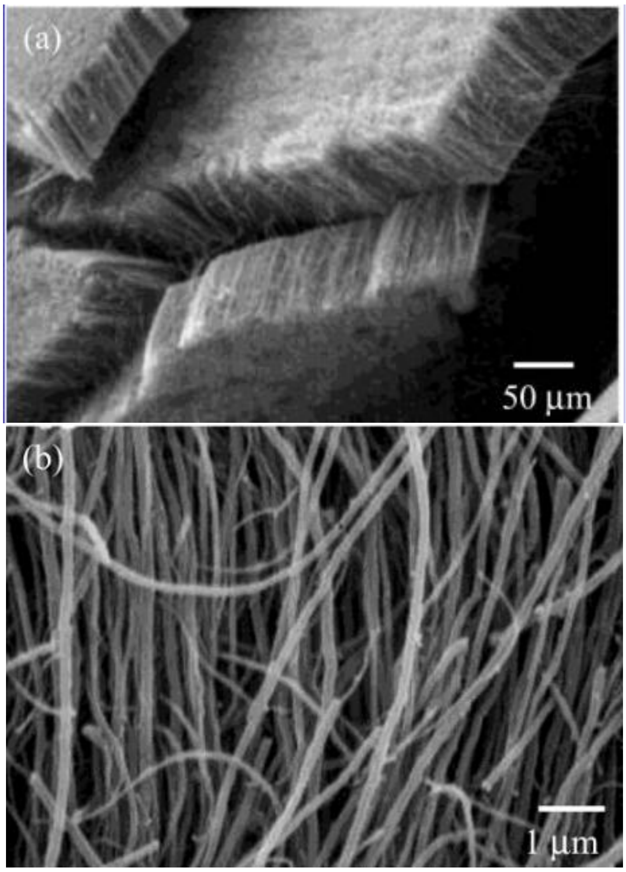

Figure 2.9: Typical well-aligned multiwall nanotube arrays from the floating catalytic CVD (Andrews et al., 1999)

Electrically conductive fillers have been added to the insulating rubber matrix to create conductive rubber composites, which have been studied. Typically, electrical conductivity provided by carbon-based fillers rises with the amount of filler loaded into the elastomer matrix (Nanda & Tripathy, 2008). In order to improve the electrical characteristics of rubber composites, carbon fillers are crucial. It should be noted that an ideal filler type can be chosen for a specific amount of electrical conductivity. Typically, carbon black or other micro-scale particles are utilised as conductive fillers to enhance the electrical or dielectric properties of rubbers (Salaeh & Nakason, 2012). However, the rubber composites with carbon black in them have a high percolation threshold concentration (i.e., the filler content required in order to form electrically conductive connected paths). Contrarily, carbon nanotubes (CNTs) are nanoscale fillers that have been employed to reinforce rubber nanocomposites to improve their electrical and mechanical properties. These nanotubes often have a high surface area to volume ratio and a very high aspect ratio (i.e., length to diameter ratio). As a result, polymer composites may be able to acquire excellent electrical conductivity from multi-wall carbon nanotubes (MWCNTs) even at low loading levels (Lee et al., 2009). The levels of electrical and dielectric properties of the filler/polymer composites are observed to be influenced by the aspect ratio and filler dispersion in a rubber matrix. Recently, researchers looked at the effects of MWCNTs' aspect ratio in poly (vinylidene fluoride) nanocomposites, which ranged from 62 to 833. The percolation threshold and the dielectric constant of MWCNTs were discovered to initially rise with the aspect ratio, but to fall after an ideal aspect ratio (Yao et al., 2007). The polycarbonate/MWCNT nanocomposites were created with two aspect ratio ranges, namely 55-134 and 134-313. It was discovered that as aspect ratios increased between 55 and 134, the percolation threshold decreased. But as the aspect ratios rose in the 134–313 range, the percolation threshold rose as well (Guo et al., 2014). The ENR/MWCNTs nanocomposites with an aspect ratio of 158 and in the range of 1,250-3,750 were utilised in the current work. The ENR nanocomposites with lower aspect ratios also showed a reduced percolation threshold. Additionally, the thermoplastic elastomer composites' frequency responses in terms of conductivity and dielectric permittivity were impacted by the MWCNTs' size (Shehzad et al., 2013). Though there has been limited research on rubber vulcanizates, the majority of these investigations have been on a thermoplastic matrix. A 250 aspect ratio EVA composite made of MWCNTs was created. The material created using the solution method showed the percolation threshold (Sohi et al., 2011). Additionally, this investigation may be the first to be conducted in a matrix made of natural rubber. Due to the high viscosity of the rubber matrix, it may still be challenging to determine the effect of filler aspect ratio on the electrical properties of rubber vulcanizates.

Inpil et al. (2011) claimed that the addition of MWCNTs improved the tensile strength, stiffness, and electrical conductivity of elastomeric composites. The highly entangled nature of as-produced MWCNTs, however, makes it challenging to obtain a homogenous dispersion of MWCNTs in polymer matrix. Due to their propensity to aggregate when reinforced with polymeric materials, CNTs have been found to negatively impact mechanical and other properties. This is brought on by the strong hydrogen bonds formed by polar functional groups on the surfaces of CNTs and the Van der Waals interactions between CNT particles. NR/CNT nanocomposites have been used in a number of works. According to Fakhru et al., it was discovered that the addition of 10 wt % CNTs raised the modulus of CNT/NR composite by up to 12 fold while lowering tensile strength and elongation at break. The addition of MWCNTs to NR was said to significantly improve the characteristics. Zheng et al. (2010) claim that the well-dispersed MWCNTs significantly increased the tensile strength of NR with minimal filler loading. According to Sanjib et al. (2008), the exfoliation of nanotubes in the elastomeric matrix increased the tensile and dynamic-mechanical properties with the addition of MWCNTs. The uniform dispersion of nanotubes within the rubber matrix must be addressed in order to take advantage of CNTs' advantages.

On the other hand, the composites were significantly weakened by the CNTs' poor dispersion and rope-like entanglements (Ajayan & Tour, 2007). To take advantage of the extraordinary reinforcement of CNTs, various preparation methods have been tried, such as solution blending, melt blending, and in situ polymerization in the case of thermoplastics (Moniruzzaman & Winey, 2006); dry mixing and wet mixing in the case of elastomers (Bokobza, 2007); and the resulting properties have been reported to be influenced by the nature of the matrix and the preparation process. Only a few efforts have been made so far with regard to elastomer/CNT nanocomposites. According to López-Manchado et al. (2004), natural rubber/single-wall CNT composites were found to have a robust filler matrix interaction. Cho and Kim (2010) have investigated the impact of the processing parameters on the surface resistivity of acrylonitrile-butadiene rubber/MWCNT nanocomposites. According to Falco et al. (2009), CNTs interfere with the vulcanization of styrene butadiene rubber because they cause the accelerators to adhere to their surface. Wet mixed MWCNTs in SSBR/BR blends have been shown to have higher alternating current (AC) and direct current (DC) electrical conductivity than dry mixes (Das et al., 2015). By using the Mullins effect, Bokobza et al. examined the amount of reinforcement produced by carbon black and MWCNTs in a natural rubber system and found that only 3.8 wt% of MWCNTs exhibit the same level of reinforcement and stress softening as 33.3 wt% of carbon black. It was studied how acrylonitrile concentration and hydrogenation affected the crosslinking density, tear strength, and elastic modulus of nitrile and hydrogenated nitrile rubber/MWCNT composites. Lorenz et al. (2009) found that the wet and dry mixed MWCNTs/silica hybrid system in natural rubber had improved fatigue crack propagation resistance. Comparing and characterising the current voltage characteristics of polydimethylsiloxane/MWCNT composites as a function of

MWCNT weight percentages (range from 0.8 to 2.5 wt.%), it was found that conductivity is low till 1.5 wt.% (Khosla & Gray, 2009). All of the investigations previously mentioned used CNTs that had not been altered by an ionic liquid.

Ionic liquids (ILs) are fluids made entirely of ions with melting points lower than 100 °C; the traditional high-temperature molten salts are excluded from this definition (Liu et al., 2008). Due to their sensitivity to oxygen and moisture, the initial generation of ILs based on chlorides did not perform effectively. The second generation ILs based on imidazolium, however, caught the interest of the entire scientific community since they are air and moisture stable. ILs may be used in electrochemical batteries, actuators, and electrochromic devices due to their distinct features (Lu et al., 2002). A chance discovery made by Fukushima et al. (2007) opens up a new avenue for IL-based CNT modification. CNT bundles get untangled after being ground into ILs, and the resulting fine bundles take on a network topology as a result of the unique interaction between the imidazolium ion component and the surface of the p-electronic nanotubes. An elastic conductor based on vinylidene fluoride-hexafluoropropylene copolymer covered with PDMS has been created for the creation of electronic integrated circuits by utilising IL modified single-wall carbon nanotubes (SWCNTs) (Sekitani, 2008). It has been reported on a work that uses ILs as a coupling agent between MWCNTs and diene elastomer.

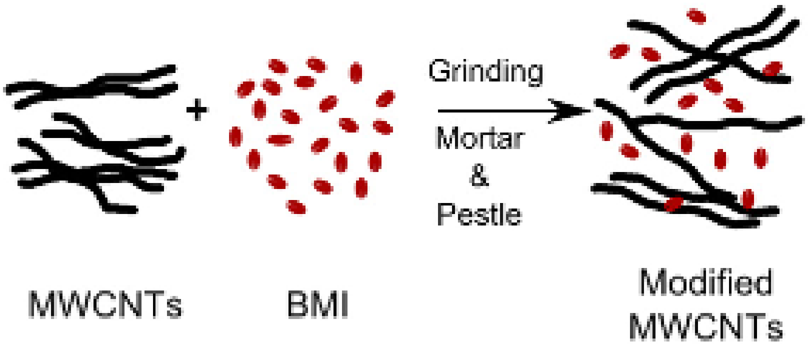

Figure 2.10: Scheme of the preparation process (Fukushima et al., 2007)