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*An Overview of the Chemical Modification of
Natural Rubber for Improved Properties and
Performance: A Systematic Review*

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Dedications

We would like to dedicate our Master-thesis:

- To our family especially our parents whose unbelievable endurance, unconditional love, and untouchable devotion have been monumental;

-To all our brothers and sisters;

-To those who will be happy with this new goal in our study career;

-To all our best friends;

- To anyone who has ever taught us anything.

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To this end, we fully take all responsibility for any mistakes that may have occurred in this work.

*Table of
Contents*

Table of contents

Contents

Dedications.....	I
Acknowledgements.....	II
Table of Contents.....	IV
List of Figures and Scheme.....	VI
List of Abbreviations.....	VII
Introduction.....	1
Chapter I An overview of Natural Rubber	
I.1 Natural Rubber.....	2
I.1.1 History.....	2
I.1.2 Chemical structure of Natural Rubber and synthesis methods.....	7
I.1.3 The unique qualities of Natural Rubber.....	10
I.1.4 Properties of Natural Rubber.....	12
I.1.5 Chemical modification of Natural Rubber.....	12
I.1.5.1 Modification by bond rearrangement.....	13
I.1.5.2 Modification by introducing a chemical group.....	16
I.1.5.3 Grafting of a polymer onto the NR backbone.....	19
I.1.6 Recycling of Natural Rubber.....	20

Table of contents

I.1.7 Applications of Natural Rubber.....	22
References.....	24
Chapter II Literature Review	
II.1 Grafting of functional groups onto natural rubber.....	25
II.2 Epoxidation of Natural Rubber.....	29
II.3 Cyclization of Natural Rubber.....	31
II.4 Hydrogenation of Natural Rubber.....	33
II.5 Vulcanization of Natural Rubber.....	35
References.....	38
conclusion.....	40
abstract.....	42

*List of
Figures*

List of figures

Figure I.1. Chemical structure of natural rubber (cis-1,4-polyisoprene).....	8
Figure I.2. Cultivated Hevea tree in a plantation under tapping operation.....	11
Figure I.3. Cyclisation of natural rubber (cis-1,4-polyisoprene).....	14
Figure I.4. Mechanism of photochemical reaction of NR induced by light.....	16
Figure I.5. Hydrogenation of NR.....	16
Figure I.6. Epoxidation of natural rubber.....	17
Figure I.7. Chlorination of NR.....	19
Figure I.8. Grafting of a second polymer onto the NR backbone.....	20
Figure I.9. Simplified schematic of typical ambient grinding and reclaim system.....	21
Figure I.10. Schematic of typical cryogenic grinding system.....	22

*List Of
Notations and
Abbreviations*

List of Abbreviations

<i>Abbreviations</i>	<i>Description</i>
NR	Natural rubber
LNR	liquid natural rubber
ENR	Epoxidized Natural Rubber
DSC	Differential Scanning Calorimeter
NR-g-MA	Graft copolymers of natural rubber and maleic anhydride
MA	Maleic anhydride
GMA	Glycidyl methacrylate
NR-g-GMA	Glycidyl methacrylate was grafted onto natural rubber
CNR	Cyclic Natural Rubber
NR-g-PAA	Poly-acrylic acid grafted natural rubber
NR-g-PVAc	vinyl acetate grafted natural rubber
FTIR	Fourier-Transform Infrared spectrometer
TGA	Thermal Gravimetric Analysis
DPNR	Deproteinized Natural Rubber
HNBR	Hydrogenated Natural Rubber

List of Abbreviations

<i>Symbols</i>	<i>Description</i>
T	the absolute temperature
σ	Tensile strength
ϵ	Strain
μm	Micrometer
min	Minute
mm	Millimeter
ml	Milliliter
$^{\circ}\text{C}$	Degree Celsius
h	Hour
N	Newton
J	Joule
η	Viscosity
wt %	Percent by weight
%	Percent
E	Young's modulus
T_m	Melting temperature ($^{\circ}\text{C}$)
T_g	Glass transition temperature
J/m	Joule per meter

List of Abbreviations

KJ/m²	Kilo Joule per square meter
T max	Temperature maximum
TG	Glass transition temperature (°C).
t	Time
ΔH_m	Melting enthalpy of sample
m	Masse
T_c	Crystallization temperature

*General
Introduction*

Introduction

Natural Rubber (NR) obtained from the *Hevea brasiliensis* tree is currently the only natural rubber resource commercially available. It is an important material in the rubber industry, particularly for the manufacture of rubber tyres, as it possesses excellent physical properties including high elasticity, high tensile strength and low heat build-up. Natural rubber also has some undesirable properties such as low heat and abrasion resistance and poor ageing properties, as well as low oil and flame resistance. These drawbacks may be due to the high unsaturation of the molecular chain and the non-polar character of natural rubber. Chemical modification of Natural Rubber has become an important method for improving the properties of NR and of widening its range of uses. It was first developed at the beginning of the nineteenth century, some 50 years earlier than the chemical modification of synthetic polymers. Having a highly cis-1,4-polyisoprenic structure, the chemical reactivity of the carbon-carbon double bond of NR is considered to be similar to that of simple olefins. The classical organic chemistry reactions of olefins may therefore be applied to NR, in particular the addition reaction with various chemical reagents (halogenation and hydrogenation), including epoxidation.

The chemical modification of NR has generally followed two directions:

- 1- Improving undesirable properties such as low heat and hydrocarbon oil resistances.
- 2- Transforming NR into new polymeric materials for specific applications such as photo-cross-linkable rubbers and thermoplastic elastomers.

Overall, this Master-Thesis is composed of two chapters. The first one presents a theoretical background and an overview of the Natural Rubber, Chemical modifications of Natural Rubber and their effects on its properties, Major applications of modified forms of NR in industrial fields. The second chapter presents a brief presentation of some of the works that have been published and which covered different aspects of the subject. The overall conclusion of this bibliographic research is discussed in the last part.

Chapter I
An overview
of Natural
Rubber

I. An overview of Natural Rubber

Natural rubber is a versatile and valuable material that has been used for centuries in a wide range of applications due to its unique properties. It is derived from the sap of *Hevea brasiliensis*, a tree that grows primarily in tropical regions. The sap, also known as latex, is collected by tapping the tree and then processed to form the rubber material. Natural rubber is highly elastic, tear-resistant, and has excellent resilience, making it ideal for use in products such as tires, rubber bands, medical devices, and many more.

In this chapter, we will provide an overview of Natural Rubber, including its history, production, properties, and uses. We will also discuss the chemical structure of Natural Rubber, the process of vulcanization, and how these factors contribute to the unique properties of the material. Overall, this chapter aims to provide a comprehensive understanding of natural rubber and its importance in our world.

I.1 Natural Rubber

I.1.1 History

Of all the wonderful tales reported by Christopher Columbus after his second voyage to the New World in **1496**, none was stranger than the story of the natives in Haiti who played with a ball made from the gum of a tree—a ball which bounced.

Before **1500**. Rubber was first found and used by Indian tribes in the New World to waterproof articles of clothing and footwear with the gum dried over smoked fires. In fact, games played with such a rubber ball are known as far back as the 11th century, throwing light on the advanced Mayan civilization.

1500: Columbus is said to have brought some of the bouncing rubber play balls back from Hispaniola (Haiti) to Queen Isabella. (Recorded in 1615 by the court historian to Philip II.)

After **1500**. While native rubber articles (play balls, bowls, bottles, hats, capes, shoes) were brought to Spain and Portugal from various parts of Central and Northern South America, no commercial use was made of rubber for nearly 300 years after Columbus.

1745. Frenchman Charles Marie et al, Condamine made a report on rubber to the Paris Academy of Sciences, the first scientific or commercial interest shown in the substance. He had been sent to Ecuador in **1735** by the Academy to survey a parallel of latitude at the

equator to see if the earth was a sphere or elongated at the poles. He crossed the continent from Quito to Para, over the Andes, and down the Amazon River in 3.5 months, coming out on the coast at Cayenne in French Guiana. He brought back a few oval hunks of what he said the natives called "cahutchu" or "weeping wood." (The French word for rubber is now "caoutchouc.") He told how natives made shoes and raincoats by dipping molds or fabrics into the juice of the Hevea tree and curing thin layers over smoky fires. But his samples wouldn't melt and no solvent was available

1763. French chemist, Macquer, and physician, Herissant, reported turpentine as a rubber solvent. But they found rubber products sticky in warm weather and brittle and hard in cold.

1768. Macquer made a pair of riding boots for Frederick the Great by coating a wax cylinder with rubber dissolved in ether. The ether evaporated and the wax melted in hot water. This was, however, too costly a method to be practical.

1770. The English chemist, Priestly, gave the name "rubber" to the raw material when he found it would "rub off" pencil marks. Ironically, in so doing he may have unawaredly become the first one to add carbon black to rubber.

1791. The first rubber patent was issued to Samuel Peal in England. It called for preparing waterproof fabrics by means of a solution of rubber in turpentine.

1811. The first rubber factory was probably established in Vienna by Johann Nepomuk Reithofer.

1813. First United States rubber patent to Jacob F. Hummel of Philadelphia for a rubber varnish to waterproof shoes.

1823. A patent was issued to Charles Macintosh in Glasgow covering a waterproof fabric of two pieces of woolen cloth held together with a naphtha-rubber dope. But "Macintosh clothing" was stiff in cold weather and had a "gas-house" odor in warm weather. Also the rubber deteriorated and the cloth peeled apart.

Thomas Hancock, a London coachmaker, became interested in Macintosh waterproofs for carriage tops and curtains. He experimented to break the naphtha patents and patented an idea of cutting rubber into long strips-elastic bands for glove wrists, pocket edges, shoe tops, etc. He was so successful that he gave up his coach business and became the first English rubber manufacturer.

1830. English developments, plus imports of uncured rubber shoes from Brazil (from about **1825**), sent many Americans into the rubber business. Much money was lost because turpentine solvent increased stickiness and deteriorated the rubber.

1839. Goodyear made his discovery of vulcanization in 1839 which introduced the great era of rubber manufacturing. He was testing the effects of heat on a rubber-sulfur compound smeared on cloth and carelessly left the sample overnight in contact with a hot stove. It charred like leather. Goodyear recognized the importance of his discovery but couldn't find a backer. He kept it a secret for 5 years.

1844. The patent on vulcanization of rubber was issued to Good- year. But the delay was costly to him because Hancock had secured the English patent rights in the meantime to sulfur-heat treatment. Goodyear put on rubber shows in London (**1851**) and Paris (**1855**), and spent much money defending patents. He patented over 200 applications of rubber-but not tires. He died in **1860**, heavily in debt.

1846. Thomas Hancock made solid rubber tires for the carriage of Queen Victoria, perhaps thereby launching our present vast tire industry.

Before 1860. The demand for natural rubber was small and most of it was collected by the Indians of the lower Amazon region. They would go into the jungle, tap the trees, collect the latex, then mold it into bottles, shoes, and "biscuits" over open smoky fires. The Indians would carry the rubber in canoes to trading towns on the Amazon, barter it for trinkets to Portuguese traders who took the rubber to Para where it was sorted, packed, and shipped. Tonnage exported from Para exceeded 1000 tons by **1850**.

1860 to 1865. Increased demand for rubber and Civil War inflation of United States currency sent the price up over a dollar a pound in 1865. This stimulated trade in the Amazon and also in Colombia and Ecuador.

1866. Don Pedro II of Brazil opened the Amazon River to ocean steamers and some went as far as 1500 miles upstream to load rubber. As demand grew and the price increased, natives were exploited, became debt-slaves, and organized into gangs on territories staked out by traders to tap, collect, and cure rubber. Many thousands of trees were killed by improper tapping.

1870. The idea of planting and cultivating the Hevea rubber tree had been suggested by both Goodyear (**1853**) and Hancock (**1857**) in their autobiographies. Interest in the idea of developing rubber plantations in the Far East grew in the early 1870s following the success of the Dutch in transplanting the quinine tree from Peru to Java and the introduction of tea into Ceylon.

1873. Dr. James Collins, curator of Physic Gardens of London Apothecaries Company, went to Brazil to obtain Hevea seeds. His first lot was shipwrecked. He eventually got out 200 seeds but only a dozen germinated in England. He sent six plants to Calcutta but all died.

1876, Collins wrote Henry Wickham, a young English coffee planter who lived in Brazil above the junction of the Tapajos and Amazon Rivers, and asked him to collect and ship several thousand Hevea seeds. Wickham got natives to collect the seeds, and packed them in wicker baskets between layers of banana leaves, hanging them up in the hold of the ship to allow air to circulate and prevent the seeds from turning rancid. On June 14 the ship docked at Liverpool and the seeds were put on a special train for Kew. Seventy thousand seeds were planted in all available nursery beds, of which 2800 germinated and **1919** young rubber plants were sent to Ceylon the following year. Of these, 90% survived the trip and were planted in botanical gardens of Paradenya and Heneratgodo where some are still alive and yielding rubber today. A few were sent to the British Resident at Perak, Malaya, Sir Hugh Low, who grew seven in gardens at Kuala Kangsar and, in **1882**, reported sending seeds and plants to Singapore, India, and Java.

1880. Between 1880 and 1900 there was a period of experimentation with plantation rubber. Actual production was small. It took 7 years from seed to tapping and required large capital investment. Different climates, locations, and methods of cultivation were tried. By **1888**, about 1000 trees were scattered throughout the Malay Peninsula. At this point a most significant step in the rubber growing industry took place. Henry Ridley took over the Singapore Gardens. Ridley demonstrated to planters that rubber trees could be grown in cleared areas in regular order, tapped frequently and economically, and the liquid latex converted to dry, clean, raw rubber ready for use. In so doing, Ridley discovered the phenomenon of "wound response" wherein latex flowed more freely after the initial tapping, that the tree could be tapped in intervals of a few days, and that the excised bark would renew itself after a few years for subsequent tapping, thereby permitting trees to yield latex

economically and efficiently for at least 30 years. In **1889**, only about half a ton of plantation rubber was produced in all the Far East.

1888. The first useful pneumatic tire was made by John Dunlop in England, making possible a new era of movement by bicycle and ushering in the new eras of motor cars.

1899. Year of first official record-4 tons of plantation rubber were produced from 4000 acres under cultivation. In **1905**, 145 tons of plantation rubber were produced from a total of 127,000 planted acres. By **1910**, production had increased to 8200 tons from 1,125,000 planted acres.

1912. Plantation rubber from Southeast Asia exceeded the output of Brazil for the first time, and 2 years later produced twice as much rubber.

1922. Southeast Asia plantations produced 93% of the world supply of rubber. By **1932** this had increased to 98%.

1920-1940. Wide fluctuations in the supply and demand for natural rubber caused great fluctuations in prices. An attempt to stabilize prices and production in the 1920s failed. Another attempt in the late 1930s was more successful but was discontinued when World War II began.

1940. The United States began stockpiling natural rubber as a strategic material as war clouds gathered. Imports into the United States in **1941** were over a million tons, about double normal prewar consumption.

1942, Japanese occupation of Southeast Asia shut off nearly 90% of the world's normal source of natural rubber. Development of synthetic rubber and the building of synthetic plants in the United States with about a million tons' capacity during World War II was one of the great examples of American engineering and production genius.

1945. Recovery of the rubber-producing areas from the Japanese found the rubber trees intact but the machinery destroyed, the plantations grown up with jungle, and the Chinese and Indian workers dispersed. Rehabilitating these plantations and getting them back into production to meet the postwar demand for natural rubber was a major achievement by the rubber growers. It was accomplished without government subsidy, aid, or control, and with natural rubber selling on a free market at prewar price levels.

1950. The post-World War II petrochemical and polymer developments were massive, and aggressive technoeconomic competition with natural rubber (NR) was the order of the day in the 1950s.

1964. Competition from synthetic rubber (SR) forced the NR industry to adopt a more outgoing and enterprising posture. Deficiencies in NR centered around presentation standards and the traditional system of visual grading. The elimination of both these drawbacks were priority objectives of the Standard Malaysian Rubber Scheme, introduced in Malaysia and later adopted by all other producing countries. Technically specified rubbers now constitute more than half of all NR produced in the world.

1970. The Association of Natural Rubber Producing Countries (ANRPC) was established comprising Malaysia, Indonesia, Singapore, Thailand, Sri Lanka, and Vietnam. This Association provided, among other things, a forum for consideration of a producer approach to bring about a stable price structure.

1973. The petroleum situation of the 1970s, the emerging strong lobbying against environmental pollution, and the growing concern of depleting nonrenewable resources introduced entirely new equations in the NR-SR interactions. While natural rubber obviously could not be thought of in terms of taking back all of the market lost to synthetics, the possibility of a move from 30% of world rubber hydrocarbon consumption to something approaching 40% presented the industry with an exciting challenge—assuming, of course, relative price stability and supply.

1979. Major producing and consuming countries reached an agreement in Geneva to stabilize world market prices and supplies of natural rubber. The arrangement, agreed to under the auspices of UNCTAD, provides for floor and ceiling prices on natural rubber and a buffer stock to be set up of 550,000 tons¹.**[1]**

I.1.2 Chemical structure of Natural Rubber and synthesis methods

Natural rubber (NR), is almost the only commercial rubber from a natural source, even though over 2,500 species of plants have also been found to produce cis-1,4-polyisoprene (**Figure I.1**). Guayule has been investigated as an alternative source of NR, which contains

resin, rubber-soluble triglycerides and higher terpenes. Guayule rubber is also made of high molecular weight cis-1,4-polyisoprene, produced and stored in the parenchyma cells, but having a narrower molecular weight distribution and physical properties slightly different from those of Hevea rubber. Among the different plant species producing rubber, *H. brasiliensis* has proved to be the best rubber producer at the present time, owing to the high productivity of the plant and excellent physical properties of the rubber product. In addition, although the cis-polyisoprene synthesized with a Ziegler catalyst has a marked structural resemblance to NR, Cultivated Hevea tree in a plantation under tapping operation. It shows considerable differences in some properties such as lower tensile strength, lower tear strength and hardness. Due to its outstanding properties, NR cannot be replaced by synthetic rubber in some specific applications such as heavy-duty tyres, gloves, condoms, etc. Furthermore, there is currently a rise in the awareness of environmental issues. NR is an interesting material made from a renewable source, while the synthetic rubber is obtained from non-renewable oil-based resources. [2]

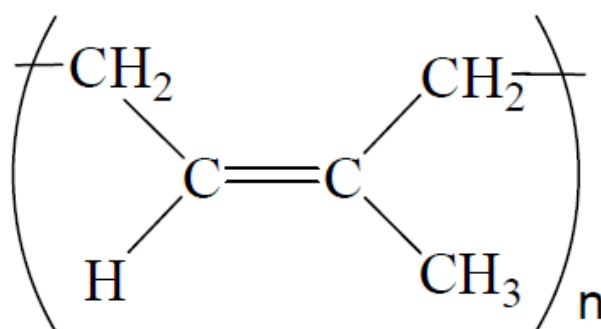


Figure I.1 Chemical structure of natural rubber (cis-1,4-polyisoprene). [7]

NR latex exuded from the Hevea trees is a colloidal suspension. Tapping frequencies around the world range from daily to every 4 or 5 days. The amount of latex obtained on each tapping depends on clones, ages, soil, climatic conditions and tapping frequency. The collected latex is usually treated with formic acid to coagulate the suspended rubber particles within the latex. After being pressed between rollers to form the rubber into 3–5 mm thick slabs or thin crepe sheets, the rubber is air- or smoke-dried at 50–60 °C for 2–3 days into a final thickness of 2–3 mm for shipment. These rubbers are known as airdried sheet (ADS) and ribbed smoked sheet (RSS), respectively. RSS is visually subdivided into six grades based on colour, consistency and observed impurities, as described in the ‘Green Book’.4 RSS No.IX is the top

grade and the subsequent grades are RSS No.1 to RSS No.5. RSS is mainly used in automobile tyre manufacturing. Latex is treated with bleaching agents to produce rubber that is pale in colour, called pale crepe. This is used in applications that require light colour and good properties such as footwear, medical supplies and adhesives. The agents used for bleaching rubber are commonly thiols, known as mercaptans, such as xylyl mercaptan ($C_8H_{10}S$), tolyl mercaptan (C_7H_8S) and sodium bisulfate ($NaHSO_3$). The coagulated rubber, after treatment, is pressed to produce 1.2–1.5 mm thick rubber sheets. The sheets are dried at low temperature (35–40°C) for 3–5 days or air dried for 5–10 days. Other commercial types of NR, known as technically specified rubbers (TSRs) in block form, are systematically graded based on technical specifications specified by the International Standards Organisation (ISO), i.e. dirt content, ash content, nitrogen content, volatile matter content, etc. The high graded TSR such as TSR L, TSR CV and TSR 5 are made directly from field latex and prepared by a carefully controlled process, while the lower ones such as TSR 10 or TSR 20 are produced from naturally coagulated cup lump. Based on these specifications, major rubber-producing countries introduced their respective standards as Standard Malaysian Rubber (SMR), Standard Thai Rubber (STR), Standard Indonesian Rubber (SIR) and Standard Vietnamese Rubber (SVR).

NR can also be exported as concentrated latex. Fresh field latex consists of 30–40% dry rubber content (DRC), the other 60–70% being mainly water containing non-rubber substances. The non-rubber components, e.g. proteins, carbohydrates, lipids and inorganic salts, vary according to clones, season and age of rubber tree. The latex collected from the plantation is preserved with ammonia (NH_3) and then undergoes continuous centrifugation to produce the concentrated NR latex containing B60% rubber, which is more uniform in composition than the preserved field latex. For long-term preservation of concentrated latex, the NH_3 content is usually raised to 0.6–0.7%; this is referred to as high ammonia (HA) preserved concentrated latex. Besides preserving the latex and maintaining the colloidal stability, the NH_3 at levels above 0.3% can act as a bactericide. Low ammonia (LA) preserved concentrated latex contains only 0.2–0.3% NH_3 in combination with secondary bactericides, such as tetramethylthiuram disulfide (TMTD) and zinc oxide (ZnO). LA latex is preferred for all applications where a deammoniation process is needed. However, TMTD is known to produce carcinogenic nitrosamines in NR latex products. Other latex grades are commercialized, such as double or multiple centrifuged latex and pre-vulcanized latex. The double or multiple centrifuged latex is highly purified by re-centrifugation for use in hygienic

products such as surgical gloves, condoms, catheters, etc. Another grade is pre-vulcanized latex, which is a semi-processed latex that does not require a compounding and post-vulcanizing operation. It is particularly used in the manufacture of dipped goods such as balloons, gloves, etc. The latex is prepared by mixing centrifuged latex concentrate with vulcanizing agents, which contain sulfur, ZnO and accelerator, under heat to cause partial crosslinking of rubber molecules. The finished products are obtained after drying to produce additional crosslinking.[2]

I.1.3 The unique qualities of Natural Rubber

Natural rubber is in wide spread daily use. It is unique among types of rubber, biopolymers and other materials in general use . Its unique qualities may be summarised as follows:

- Among rubbers, it is the only biomass . All other rubbers are chemically synthesised. Natural rubber is extracted from a tropical plant in which the cis-1,4-polyisoprene molecule is bio-synthesised.
- It is the only polymeric hydrocarbon among biopolymers, i.e, cis-1,4- polyisoprene is composed of carbon and hydrogen atoms alone. All other biopolymers contain other covalently bonded elements (not as impurities) such as nitrogen, oxygen, sulphur, in addition to carbon and hydrogen.
- A biopolymer may be obtained from a variety of natural sources, i.e., plants, animals or fungi. However, natural rubber is obtained almost entirely from a tropical plant, *Hevea brasiliensis*. Its natural habitat is the Amazon River valley, but at present, 99% of natural rubber is obtained from domesticated *Hevea* trees in Asia. **Figure I.2** shows a *Hevea* tree under cultivation. By means of tapping (making a cut in the trunk), latex (a milky liquid containing rubber molecules) is exuded and drops into a cup. The latex is collected and used in its original form or coagulated to give a solid natural rubber.
- Chemical synthesis of natural rubber has not yet been established, although many industrially valuable biopolymers have been successfully synthesised by chemists
- As it is an agricultural product, natural rubber is renewable.
- It is carbon neutral, as are many plant products. The initiating material for the bio-synthesis of natural rubber is carbon dioxide, thus making it carbon neutral. It therefore does not contribute to global warming .At the end of its life; it decomposes to carbon dioxide, so there is no net increase of the gas.

- Natural rubber will remain available despite the depletion of petroleum and is expected to contribute to sustainable development throughout the twenty-first century . This is of particular importance in organic industrial materials.
- Natural rubber is scientifically unique because of its elasticity. From the thermodynamics viewpoint, this is due to an entropy change resembling that of ideal gas. It differs from energetic elasticity and standard organic, inorganic or metallic solid materials Modified Forms of Natural Rubber
- Due to its unique elasticity, natural rubber has become an essential material for automobile tyres, and has historically contributed to a society characterised by high-density transportation networks[3]



Figure I.2: Cultivated Hevea tree in a plantation under tapping operation.[7]

I.1.4 Properties of Natural Rubber

NR is an important elastomeric material, used in around 70% of all tyres and in a variety of applications in the engineering, medical, sport and household sectors. This is due to its outstanding properties which cannot be matched by the synthetic polyisoprene (IR). Before the vulcanization process, NR is not sufficiently elastic and strong to be used as such. Unvulcanised NR also becomes very soft and sticky with an increase in temperature and hard and brittle at cold temperatures. Vulcanization makes the rubber elastic instead of plastic by forming sulfur links between the rubber chains. The advantages of vulcanized NR are

- Excellent tensile and tear strength;
- Low hysteresis and high fatigue resistance;
- High abrasion resistance;
- Good rebound and compression set;
- Excellent adhesion to metal and fabrics;
- Good dielectric strength and electrical insulation.[4]

I.1.5 Chemical modification of Natural Rubber

In this part, various types of chemically modified natural rubbers (modified NRs) are reviewed in terms of their preparation, physical, chemical and mechanical properties and their potential applications. These NR derivatives include liquid natural rubber (LNR), cyclized natural rubber, deproteinized natural rubber (DPNR), chlorinated natural rubber (CNR), epoxidized natural rubber (ENR), styrene-grafted NR (SNR) and methyl methacrylate- grafted NR.

Commercial natural rubber (NR) or cis-1,4-polyisoprene is obtained from *Hevea brasiliensis*. The NR latex, which is exuded from *H. brasiliensis* bark, is processed in either wet or dry form. Rubber bale is obtained from either field latex or coagulum. The field latex will be coagulated, formed into crepe, dried and packed. Commercial NRs are graded based on dirt content, ash content, nitrogen content, volatile matter content, etc. as specified by International Standards Organisation (ISO). The technically specified rubbers were first introduced into the market by Malaysia in 1965 as the Standard Malaysian Rubbers (SMRs). Currently, commercial NRs are also specified according to Standard Thailand Rubber (STR), Standard Indonesian Rubber (SIR) and Standard Vietnam Rubber (SVR). Due to the high molecular weight of NR as well as its low glass transition temperature (T_g), NR vulcanizes

are elastic with high tensile strength and low heat build-up. However, due to the presence of allylic carbons, the vulcanizates have poor abrasion, ageing and weathering resistance. These drawbacks can be overcome by chemical modifications of NR. In chemical modifications, changes in molecular structure occurred. Some examples of chemical modifications are hydrogenation and grafting.

Chemical modifications on NR can be carried out in either solid, solution or latex state. The modifications can be categorized into three categories:

- Modification by bond rearrangement without introducing new atoms. This type of modification will lead to changes in the chemical structure and/or reduction in molecular weight of NR. Cyclization is an example of bond rearrangement.
- Modification by introducing a chemical group such as hydrogen, chloride or epoxy via addition or substitution reactions at the olefinic double bonds. The resultant
- Modified NR will possess the properties of the new chemical groups. For example, epoxidation of NR results in higher T_g and mechanical properties as well as higher hydrophilicity. Modification by grafting with one or two molecules, usually vinyl monomers at the allylic carbon. The new grafted polymer can either have low or high molecular weight. The degree of grafting and degree of polymerization measure the efficiency of the modification. Grafting of methyl methacrylate (MMA) onto NR; commercially known as Heveaplus MG results in harder and stiffer copolymer. [7]

I.1.5.1 Modification by bond rearrangement

- ***Cyclization reaction***

Cyclization is the simplest and earliest chemical modification of NR, Cyclization can be carried out by treating NR with a proton donor. Examples of the proton donors are sulphuric acid, sulphonic acid, stannic chloride and acid hydrochloric. Modification can be carried out either in solution or in solid or emulsion form. For modification in emulsion state, destabilization of the NR latex is crucial and Lewis acid is not suitable. **Figure I.3** shows the cyclization mechanism of NR.

Recently, cyclization on deproteinized natural rubber (DPNR) latex was reported by Riyajan et al. Cyclization on DPNR was reported to be more effective as the presence of the protein can retard and disturb the chemical modification. Cyclized NR in general was reported to be tough, hard and brittle but some elastic behaviour is still maintained. The T_g of cyclized NR increases with higher cyclization where the degree of cyclization is measured from unsaturation of the cyclized NR. For example, the elastomeric behaviour is retained at 30%

cyclization but at 60% cyclization, it has a leather-like characteristic. Cyclization up to 90% resulted in a powdery form material indicating high brittleness. Cyclized NR is used as adhesives, printing ink as well as paints.[7]

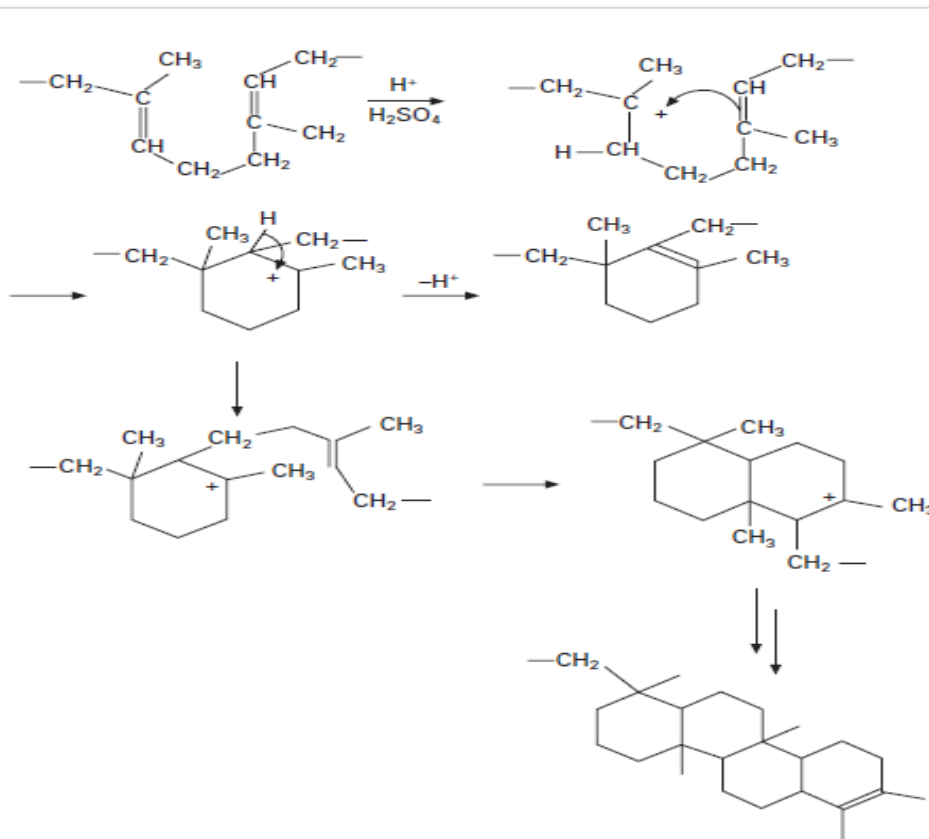


Figure I.3 Cyclisation of natural rubber (cis-1,4-polyisoprene). [7]

- **Liquid Natural Rubber**

Liquid natural rubber (LNR) can be derived from depolymerization of NR. The initial objective to prepare LNR was to reduce the internal viscosity of NR. NR with lower viscosity facilitates the addition of additives. This can be achieved via mechanical shearing using either two roll mill or internal mixer. Depending on the milling time and temperature, the average molecular weight in the range of 400,000–1,000,000 Da was achieved. LNR with reactive terminal groups received high attention by researchers as the terminal groups can undergo further chemical reaction or take part during vulcanization. LNR with reactive terminal groups can be prepared via redox couples, photochemical or oxidation. Different preparation methods yield different molecular weights. The oxidation approach yields lowest number average molecular weight, M_n ; that is, 2500–3000 Da while the redox couples approach reported M_n in the range of 3000–35,000 Da. The photochemical approach received high attention from researchers. Its range of M_n is of 3000–8400 Da. The only LNR obtained from

oxidation is the hydroxyl-terminated LNR. It was prepared by depolymerizing masticated NR in toluene solution under pressure of 200–300 psi and temperature of 150°C with the presence of hydrogen peroxide. LNR prepared via redox couples used both oxidizing and reducing agents either in solution or in emulsion state. LNR with hydroxyl or carbonyl or phenylhydrazone terminal groups was prepared using either hydrogen peroxide or organic peroxide/sulphanilic acid or phenylhydrazine, or phenylhydrazine/ ferric chloride/oxygen, or phenyl hydrazine/oxygen. Photochemistry of NR was achieved by ultraviolet (UV) light or sunlight in the presence of compounds such as nitrobenzene and hydrogen peroxide. The former compound will produce carboxyl-terminated LNR, while the latter compound hydroxyl-terminated LNR. **Figure I.4** shows an example of light-induced photochemical approach in producing hydroxyl-terminated LNR. Free radicals formed from the bond cleavage under either sunlight or UV light will lead to depolymerization of NR.

Metathesis of NR is a reaction which can induce the cleavage and reforming of the double bonds as well as exchange of substituents in depolymerization of NR. A study by Alimuniar et al. shows that cyclic oligomer of isoprene was produced from intra- and inter-molecular reaction by using tungsten hexachloride and tetramethyl tin in chlorobenzene with purified NR. Depending on the reaction temperature and duration, the molecular weight was in the range of 5800–110,000 Da.

Natural Rubber and its Derivatives 161 LNR can be used as viscosity modifier, adhesive, tackifier, sealing agent, plasticizer as well as compatibilizer. LNR was reported to be a good compatibilizer in linear low-density polyethylene/natural rubber (LLDPE/NR) blends, polypropylene/natural rubber (PP/NR) blends, high-density polyethylene/natural rubber (HDPE/NR) blends and low-density polyethylene/natural rubber (LDPE/NR) blends. The presence of LNR in HDPE/NR blend changed the morphology from co-continuous to dispersed phase suggesting better degree of compatibility. The tensile strength and elongation at break results were reported to be consistent with the morphological analysis . .[7]

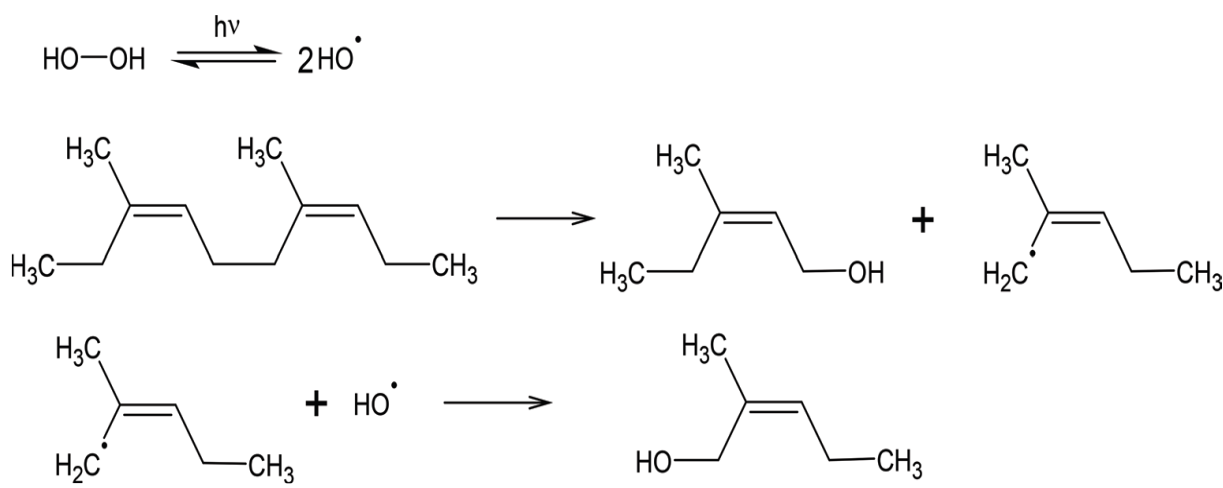


Figure I.4. Mechanism of photochemical reaction of NR induced by light[7]

I.1.5.2 Modification by introducing a chemical group

- **Hydrogenated Natural Rubber**

Hydrogenation of natural rubber is still a scientific curiosity. Fully hydrogenated natural rubber, due to the removal of its unsaturation is unaffected by chemical reagents that normally attack unmodified natural rubber. However, the fully hydrogenated natural rubber cannot be vulcanized in the conventional manner. Platinum black was used as the catalyst for the production of hydrogenated rubber $(\text{C}_5\text{H}_{10})_x$ from dilute solutions of purified rubber. More recently Burfield et al. achieved complete hydrogenation in solution after one hour at 28°C using homogeneous two component catalyst systems based on a variety of nickel and cobalt compounds in combination with triisobutylaluminum. Potential applications considered for hydrogenated natural rubber are in the cable industry, and for the preparation of adhesive compositions. [6]

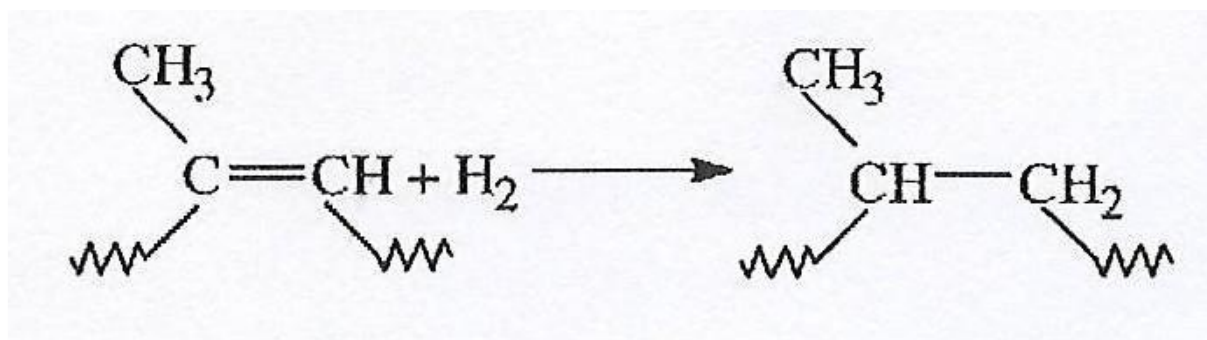


Figure I.5 Hydrogenation of NR. [6]

- **Epoxidation Natural Rubber**

Epoxidation of NR is a recognized technique to improve the properties of the rubber such as solvent resistance, hydrocarbon oil resistance and gas permeability and to increase damping, while retaining the high tensile strength and tear strength of NR. Epoxidation of NR was first carried out in 1922 by Pummerer and Bukhard. The reaction proceeds by addition of an oxygen atom to the carbon-carbon double bonds on the NR backbone to form an oxirane (epoxide) ring. The epoxidation has been mainly performed in latex form using a prepared peracetic acid, performic acid, or a mixture of hydrogen peroxide and an organic acid, i.e. formic acid or acetic acid. The NR modified by this reaction is called epoxidized NR (ENR). The properties of ENR depend on the degree of epoxidation, which is controlled by the amount of peracid, reaction time and temperature. Two grades of ENR, ENR-25 and ENR-50, are commercially available, with 25 and 50 mol % of epoxide content. The epoxy groups of ENR were reported to be stable under controlled conditions. The ring opening and ring expanding of epoxide groups was observed under conditions of excess amounts of formic acid and hydrogen peroxide. Due to the fact that ENR is a reactive elastomer having epoxide groups, it can be used to modify properties of other polymers by blending. [2]

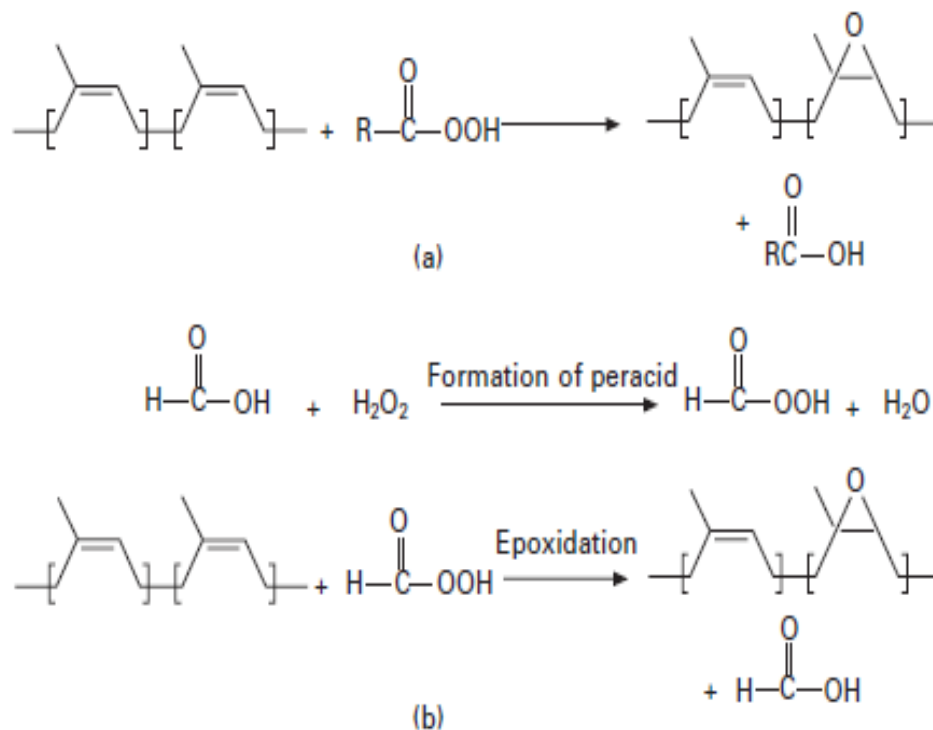


Figure I .6 Epoxidation of natural rubber (a) using preformed peracid (RCO_3H) and (b) using in-situ performic acid generated from the reaction of formic acid (HCOOH) and hydrogen peroxide (H_2O_2). [2]

- **Chlorinated Natural Rubber**

Chlorination is one of the early methods of chemical modification of NR. Chlorinated NR (CNR) shows an improvement over the properties of NR such as chemical resistance, flame resistance and thermal stability. Accordingly,

CNR has been used as a raw material for paints, adhesives, inks, coatings, etc.

The chemical modification of NR by chlorination can be done in solution or latex form. The chlorination of NR in solution form has conventionally been carried out by dissolving in CCl₄. However, this has been prohibited in many countries due to serious problems such as environmental pollution, solvent toxicity and the high equipment investment needed. Preparing CNR in latex is an alternative method. The chlorination of NR can be performed directly in latex form under conditions that stabilize the NR particles with non-ionic surfactant. Since the NR molecules exist in the rubber particles, the chlorination process in latex form is more difficult than that in solution form, when the reaction occur directly to the NR chains. Chlorination is also carried out to modify the NR surface of finished products. It produces chemical and physical changes on the modified surface, for example improving oil resistance, and reducing the tackiness and frictional resistance in household NR gloves. Many techniques such as plasma chlorination, acidified hypochlorite solution, chloramines solution and trichloroisocyanuric acid solution have been used to modify the NR surface.

The treatment is usually performed using acidified hypochlorite. It was reported that undesirable reactions, e.g. cyclization and chain scission, may also occur. However, the cyclized structures of the NR molecules are absent in the case of NR latex films chlorinated in the aqueous phase. [2]

Chlorination of NR can be carried out in solution or emulsion forms in the presence of gaseous chlorine. Four reactions of chlorination of NR are addition, substitution, cyclization and crosslinking, and are shown in **Figure I.7**.

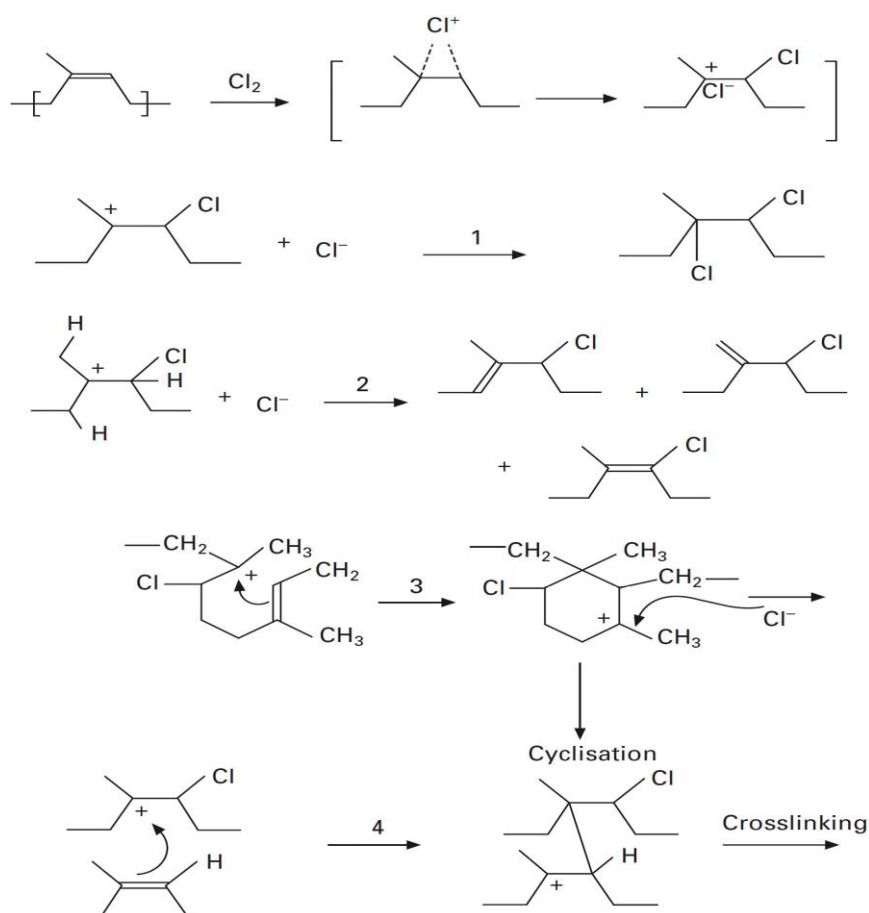


Figure I.7 Chlorination of NR: (1) addition of chlorine, (2) substitution chlorination, (3) cyclization, (4) crosslinking [2]

I.1.5.3 Grafting of a polymer onto the NR backbone

Grafting has been frequently performed using vinyl monomers like methyl methacrylate and styrene. Graft copolymers of NR and poly(methyl methacrylate) (NR-g-PMMA) known as Heveaplus MG, are commercially available in two grades: 30 % (MG 30) and 49 % (MG49) of PMMA . Heveaplus MG shows superior properties like hardness, modulus, abrasion, electrical resistance, and light color. It has been used to improve the impact properties of polystyrene, and to blend with NR as reinforcing agent. The solution or latex form of Heveaplus MG was used as adhesive or bonding agent to bond rubber to poly(vinyl chloride) (PVC), leather, textiles, and metals. Recently, Derouet et al , synthesized well-defined NR-g-PMMA by MMA photopolymerization initiated from N, N-diethyldithiocarbamate functions previously created along the NR chains **Figure I.8**. They found that the thermal stability of NR was improved after the introduction of PMMA grafts onto NR chains.[8]

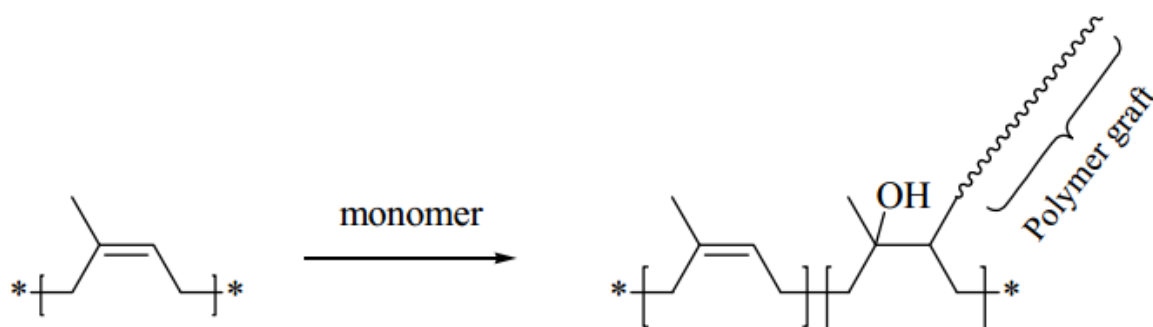


Figure I.8. Grafting of a second polymer onto the NR backbone [8]

I.1.6 Recycling of Natural Rubber

Reuse of tires and other industrial rubber products has been directed toward their use as fuel. Excluding the tires that go to landfills or to stockpiles or other storage facilities, 61% were used for fuel. The balance were recycled into other uses. Retreading of aircraft and commercial truck tires is probably the most ideal use of worn products. In the case of aircraft tires, up to four or five retreads are possible. For commercial truck tires from size 9.00R20 up to 12.00R24 or 315/80R22.5, two retreads are not unusual.

The major methods for recycling existing rubber are ambient grinding, cryogenic grinding, and wet grinding. The resulting products are useful for controlling compound cost and improve processing when added to newly compounded rubbers.

In ambient grinding, vulcanized scrap rubber is first reduced to chips on the order of 1–2 in. in size. For some rubber products such as tires, this is normally accomplished by shredding. The shredded rubber is then passed over magnetic, mechanical, and pneumatic separators to remove metals and fibers. These pieces can be reduced in size by further ambient grinding on mills or by freezing them with liquid nitrogen and then grinding them into fine particles. The ambient process uses conventional high-powered mills with close nips that shear the rubber and grind it into small particles. It is common to produce 10–40 mesh material using this method, and the material is the least expensive to produce. The finer the desired particle, the longer the rubber is kept on the mill. Alternatively, multiple grinds can be used to reduce the particle size. Any fiber and extraneous material must be removed using an air separator. Steel wires are removed by using a magnetic separator.

A flow chart for an ambient grind process including a side stream for reclaiming is shown in **Figure I.9**. The process produces a material with an irregular jagged particle shape. In addition, the process generates a significant amount of heat in the rubber during processing. Excess heat can degrade the rubber, and efficient cooling systems are essential. [9]

Cryogenic grinding uses rubber particles of up to 2 in. and freezes them with liquid nitrogen. The frozen pellets are passed into a mill for further grinding. The size of particles typically produced by this method ranges from

60 mesh to 80 mesh. The advantages of this technique are that

- 1) Little heat is generated so there is no thermal degradation of the material such as is found with ambient grinding and
- 2) Finer particles are obtained.

The cryogenic process produces fractured surfaces. The most significant feature of the process is that almost all fiber or steel is liberated from the rubber, resulting in a high yield of usable product. The cost of liquid nitrogen has dropped significantly, and cryogenically ground rubber can now compete on a large scale with ambient ground products. A flow chart for a typical cryogenic process is shown in **Figure I .10**.

Many manufacturing organizations wish to incorporate their scrap back into original rubber compound formula. This eliminates scrap disposal, provides better control over cost, and is an environmentally sound business practice. However, several practical problems arise in doing this. First, it may be difficult to accumulate sufficient clean scrap of a given compound or classification type. This is a significant drawback owing to the desire to attain consistent properties and performance of the final compound formulation. A second problem is the need for a recycling organization capable of working with small quantities of a given lot of waste material and keeping it in suitably clean condition. A third is that it is necessary to understand the effects of mesh size and concentration on the rubber properties. [9]

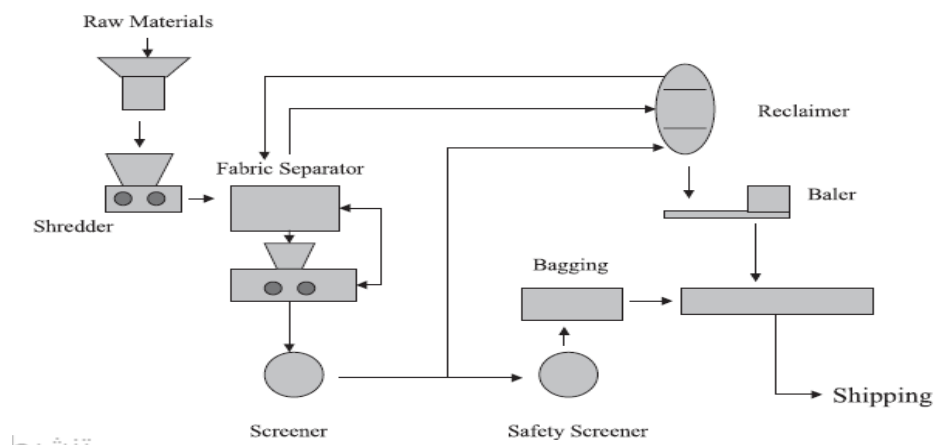


Figure I. 9 Simplified schematic of typical ambient grinding and reclaim system. [9]

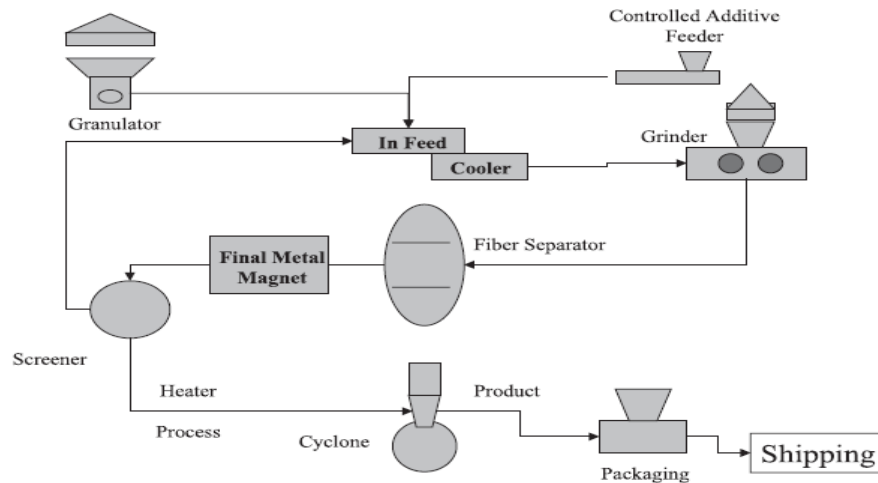


Figure I.10 Schematic of typical cryogenic grinding system. [9]

- **Compounding Application of Recycled Materials**

Recycled material can be added to the original compound formulation in one of two ways. The total elastomer content can be kept at 100 RHC, or the recycle content can be added on top of the original elastomer as filler.

Though at low levels there can be deterioration in the mechanical properties of a compound, there are still a wide variety of successful applications. For example

1. In cement and concrete the addition of recycled rubber reduces vibration transmission, improves fracture resistance, and reduces cracking.
2. In fill for sludge treatment plants, crumb rubber is effective at absorbing heavy metals and organic solvents such as benzene, toluene, and other organic solvents.
3. Asphalt containing crumb rubber is more durable, has better resistance to thermal and reflective cracking, reduces the level of noise generated by vehicles traveling on it, and provides a more comfortable ride.
4. Flooring, walkway tiles, and sports surfaces such as running or jogging tracks constitute a growing market for recycled rubber.

Such surfaces are very effective. However, the most important technical issue is removal of all steel from the material. Cryogenic grinding is typically used to produce materials for such applications. [9]

I.1.7 Applications of Natural Rubber

Owing to its excellent properties, NR is an essential component of many products used in various applications. Rubber products can be classified into six sectors as follows :

1. Tyre products: Major products of dry NR for over 70% of NR consumption is used in tyres, especially heavy-duty tyres for trucks, buses and airplanes, and tyre

products, such as pneumatic tyres and inner tubes for automotive use. The ability of NR to resist heat build-up makes the heavy-duty tyres much safer than those made from synthetic rubber.

2. Moulded products: Prepared by compression or injection of rubber compound into a closed mould. Typical products are sponges, carpet underlay, sandals, shoes, rubber bands, connectors, curing tubes, curing flaps, lining mats, o-rings, rollers, bumpers, heavy-duty pads, seals, gaskets and wheels.
3. Extruded products: Rubber is extruded through dies to form various shapes and profiles. Examples of extruded products are hoses, pipes, electric cables, refrigerator seals, window/door seals, insulators, rollers and erasers.
4. Calendered products: Calendered rubber sheets are widely used in various applications such as conveyer belts, bumpers, gaskets, roll coverings, brake linings, seals and tyre patches.
5. Adhesives: Solution adhesives consist of a mixture of solid rubber and other components dissolved in a solvent. Several adhesive systems are used to produce pressure-sensitive adhesives. The applications of solid NR are adhesives, electrical insulation tapes, adhesive tapes, packaging tapes, surgical tapes and plasters.
6. NR latex based products: The products can be classified, based on the manufacturing process, into products produced via dipping, coating and binding, foaming and extrusion processes.
 - 6.1. Dipped products such as household and medical gloves, nipples, condoms, finger caps, balloons, sporting goods and so on.
 - 6.2. Coating and binding products used for carpet backings, adhesives, adhesive tapes, self-seal envelopes, etc.
 - 6.3. Foam products such as foam cushions, foam seating, foam mattresses and pillows, etc.
 - 6.4. Extrusion products such as the elastic thread used in undergarments and socks.[9]

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Chapter II

Literature

Review

II. Literature Review

Chemical modification of natural rubber is the process of introducing chemical groups or molecules into the polymer chain of natural rubber to alter its physical, mechanical, and chemical properties. Some common methods of chemical modification of natural rubber include:

1. Grafting: This is a process of introducing functional groups onto the polymer chain of natural rubber, resulting in improved compatibility with other materials and improved mechanical properties.

Overall, chemical modification of natural rubber can enhance its performance and broaden its range of applications in various industries, including automotive, construction, and medical.

In this part and for the sake of illustration, a brief presentation of some of the works that have been published and which covered different aspects of the subject, will be made.

These studies are presented in the above listed order.

2. Epoxidation: This is a process of introducing epoxy groups into the polymer chain of natural rubber, resulting in improved resistance to oxidation, improved mechanical properties, and enhancing the interfacial interaction with the other polymer phases.

3. Cyclization: This is a process of introducing acyl groups into the polymer chain of natural rubber, resulting in improved solubility and compatibility with other materials.

4. Hydrogenation: This is a process of adding hydrogen to the double bonds of natural rubber, resulting in improved heat resistance and stability.

5. Vulcanization: This is a process of heating natural rubber with sulfur to crosslink the polymer chains, resulting in improved mechanical properties such as increased strength and durability.

II.1 Grafting of functional groups onto Natural Rubber

Grafting of functional groups onto natural rubber is a process of introducing additional chemical and functional groups onto the polymer chain of natural rubber to improve its properties such as: Mechanical; Thermal, and Dynamic mechanical properties. This can be achieved through various methods, such as radiation-induced grafting, chemical grafting, or enzymatic grafting.

In radiation-induced grafting, natural rubber is irradiated with high-energy radiation, such as gamma rays or electron beams, which creates free radicals on the polymer chain. These free radicals can then react with functional monomers, such as acrylic acid, to form a graft copolymer of natural rubber and the functional monomer.

In chemical grafting, natural rubber is reacted with a functional monomer in the presence of a catalyst to form a graft copolymer. Some common functional monomers used in chemical grafting include **maleic anhydride**, **glycidyl methacrylate**, **acrylic acid** and **vinyl acetate**.

Enzymatic grafting involves using enzymes to catalyze the reaction between natural rubber and a functional monomer. For example, lipase enzymes can be used to catalyze the reaction between natural rubber and acrylate or methacrylate monomers.

The grafting of functional groups onto natural rubber can improve its properties, such as its compatibility with other materials, its mechanical strength, and its resistance to heat, chemicals, and UV radiation. This makes it suitable for various applications, such as in the production of adhesives, coatings, and composites.

For example; **C. Nakason et al [1]**, have studied the effect of grafting of maleic anhydride (MA) onto natural rubber in the thermal properties. The thermal properties were investigated by means of Differential Scanning Calorimeter (DSC). Graft copolymers of natural rubber and maleic anhydride (NR-g-MA) or maleated natural rubber (MNR) were synthesized in a toluene solution. Benzoyl peroxide (BPO) was used to initiate the free radical graft copolymerization. Influence of monomer and initiator concentrations together with effect of the reaction temperature and reaction time were investigated. Quantities of the grafted anhydride (MA) were determined by titration of the carboxylic acid functions derived from the anhydride functions. They have found that the grafted MA level was performed using IR absorbance ratio of the peaks at $1780\text{--}1784\text{ cm}^{-1}$ plus 1854 cm^{-1} to 835 cm^{-1} . They have also found that the quantities of the grafted MA on NR molecules increase with increasing monomer and initiator concentrations. The increase in reaction time and reaction temperature also causes increasing levels of the grafted MA. In their results, they found that the glass transition temperature of the MNR was higher than that of the neat NR. Furthermore, the T_g values increase with increasing the monomer concentration used in the graft copolymerization.

In another publication, **M.S. Siregar and co-workers [2]** have investigated the effect of Trimethylol Propane Triacrylate in the grafting of Maleic Anhydride onto Cyclized Natural Rubber in the melt state. The grafting product of maleic anhydride onto cyclized natural rubber have been produced in the presence of trimethylol propane triacrylate comonomer which is processed in an internal mixer at temperature of 150°C and at a rotor speed of 80 rpm. The ratio of Tris / maleic anhydride used is 1: 2; 1: 1 and 2: 1. All grafted product was purified to determine the degree of grafting for each graft product by the titration method. From their results, they found that the degree of grafting increases with increasing trimethylol

propane triacrylate mole ratio. The highest degree of grafting is obtained in moles ratio of 2: 1 which is to 5.88%.

In another study, Glycidyl methacrylate (GMA) was grafted onto natural rubber (NR) using emulsion polymerization method and reported by **Punmanee Juntuek** et al [3]. The structures of copolymers were characterized by proton ^1H nuclear magnetic resonance (^1H -NMR), solid state, as well as ^{13}C -NMR spectroscopy, and Fourier transform infrared (FTIR) spectrometer. The mechanical properties of the copolymers were also investigated by means of tensile test. The % grafting obtained from the gravimetric method and the absorbance ratio was compared. Effects of reaction temperature, GMA content, and reaction time on % grafting, grafting efficiency, and %conversion of GMA monomer were determined. FTIR analysis and NMR results indicated the occurrence of grafting reaction in NR-g-GMA sample. Effect of % grafting on mechanical properties of the graft copolymer was studied. Experimental result showed that the appropriate reaction time was 8 h at a reaction temperature of 30°C . Moreover, tensile strength and young's modulus of the graft copolymer increased with increasing % grafting while elongation at break decreased.

In another publication, Addition of divinyl benzene comonomer to glycidyl methacrylate grafting to cyclic natural rubber was reported by **Z Alfian et al** [4]. The process of thermally grafting glycidyl methacrylate (GMA) on cyclic natural rubber (CNR) compared to the addition of an initiator of organic peroxide, dicumyl peroxide (DCP) and using cross-linker divinyl benzene (DVB) has been carried out by means of melt processing. The main aims of the modified GMA grafted to CNR was to increase the polarity of the polymer to be used as a compatibilizer agent in polymer blends. The addition of DVB co-monomer in the processing was to increase the amount of GMA implanted in cyclic rubber as measured by the degree of GMA grafting. The grafting method was carried out by melting polymer (melt processing) at high temperatures in the reactor internal mixer (Brabender plastic order model). The grafting reaction took place at a temperature of 160°C , 60 rpm rotor speed and rotation and for mixing time of 10 minutes. To determine the GMA grafting reaction on cyclic rubber, characterization was carried out with Fourier Transformed InfraRed (FT-IR) spectroscopy while the degree of GMA grafting on natural rubber was determined by acid-base titration method in organic reagents (solvents). It was found that the GMA grafting process on cyclic natural rubber could easily occur in the melting phase at high temperatures and increase with the addition of dicumyl peroxide (DCP) peroxide. Although the addition of divinyl benzene (DVB) co-monomer can increase the degree of grafting of GMA onto CNR, the addition of co-monomer can cause high cross-linking.

In another study, Synthesis method, Preparation process, properties as well as slow release characteristics of Poly-acrylic acid grafted natural rubber (NR-g-PAA) was investigated by several researchers including **Yanjun Cui et al [5]**. Firstly, NR was grafted with poly-acrylic acid by in-situ radical solution polymerization to synthesize poly-acrylic acid grafted natural rubber (NR-g-PAA), the reaction conditions were optimized to increase the water absorption properties of NR-g-PAA. Through a series of characterization and test, the structure, morphology, thermal properties and biodegradability of NR-g-PAA were determined. Subsequently, a multi-nutrient fertilizer core was fabricated with urea, KH_2PO_4 , and attapulgite by pan granulation. Then the fertilizer core was coated by NR as the inner layer and NR-g-PAA as the outer layer. Meanwhile, the slow release behaviour of the compound fertilizer in soil was also studied. Results showed that the maximum water absorbency of NR-g-PAA is $744.00 \pm 14.38\%$. The release rate of N, P and K in 30 days for NR/NR-g-PAA coated fertilizer was about $54.35 \pm 1.49\%$, $51.18 \pm 2.15\%$ and $44.37 \pm 1.38\%$, respectively, showing that the nutrient element release can last for N30 days. Overall, the novel method introduced in this study can inform the development of NR based controlled release fertilizers. They have also found that the grafted NR had lower peak than pure NR, indicating lower degradation rate for the grafted copolymers. **The thermal stability of grafted NR exhibited higher decomposition temperature and lower degradation rate than pure NR** because the increase in chemical interaction between the functional groups present in the grafted copolymer and lower unsaturated chain in its structure. More energy is required to decompose the grafted NR and hence it provides better thermal stability.

In another paper, **A. Porntrairat and C. Pattamaprom [6]** have investigated the preparation of vinyl acetate grafted natural rubber by irradiation method. Improvement in properties of natural rubber could be done by several methods. In their study, gamma radiation technique, which is simple, accurate, easy to control and clean, was applied to enhance the properties of natural rubber (NR) in latex state. The purpose of their research work is to study the appropriate condition for preparing grafted natural rubber latex by using irradiation method. Vinyl acetate monomers (VAc) were grafted onto natural rubber latex (NR-g-PVAc) at 0-10 kGys by gamma radiation from Cobalt-60 source at room temperature. Physical properties of grafted natural rubber such as chloroform number, swelling ratio and gel content were measured by means of swelling index as well as by dissolving irradiation-grafted rubber in toluene at room temperature for 72 hours, respectively. The VAc content of NR-g-PVAc was investigated by titration and visualized by FTIR spectroscopy. The FTIR spectra of NR-g-PVAc prepared at 0-10 kGys showed characteristic peaks of the vinyl acetate

confirming that VAc could be grafted onto natural rubber molecular chains effectively under appropriate irradiation conditions. The physical properties of irradiation-grafted rubber (NRG) showed that the higher irradiation dose caused the reduction in the amount of free NR, implying that some reactions took place within the rubber structure. The increase in gel content and the reduction in the percentage of free PVAc indicated that the reactions that took place within the rubber structure were both crosslinking of NR and grafting of PVAc onto NR molecules. From the result, radiation grafting was found to be a useful technique for grafting of vinyl acetate onto natural rubber.

II.2 Epoxidation of Natural Rubber

The Epoxidation of natural rubber involves the introduction of epoxide groups into the polymer chain. Epoxidized natural rubber (ENR) is obtained by the reaction of natural rubber with an epoxidizing agent, typically peroxy acetic acid or peroxy mono-sulfuric acid. This process results in the formation of epoxy groups (oxirane rings) along the rubber polymer backbone.

Epoxidation of natural rubber is typically carried out by dissolving the rubber in a suitable solvent, such as toluene or xylene, and adding the epoxidizing agent. The reaction is usually performed at an elevated temperature for a specific period of time, often in the presence of a catalyst or promoter to enhance the reaction rate.

The Epoxidation reaction proceeds through the attack of the epoxidizing agent on the double bonds present in the rubber polymer chain. The peroxy acetic acid or peroxy mono-sulfuric acid reacts with the double bond, forming an intermediate ester or sulfate, respectively. This intermediate then undergoes a rearrangement reaction, resulting in the formation of an epoxy group.

Epoxidized natural rubber possesses unique properties compared to unmodified natural rubber. The introduction of epoxy groups increases the reactivity of the rubber and allows for further modification through cross-linking or functionalization reactions. ENR exhibits improved compatibility with various polymer matrices, enhanced thermal stability, and increased resistance to heat, oils, and chemicals.

Epoxidized natural rubber finds applications in various industries, including adhesives, coatings, sealants, and elastomers. It can be used as a toughening agent for epoxy resins, a modifier for thermoplastics, or as a base material for specialty rubber products.

It's worth noting that while the Epoxidation of natural rubber is a well-established process, specific reaction conditions, catalysts, and epoxidizing agents may vary depending on the

desired properties of the final product. It is always recommended to consult the literature or seek expert advice when performing chemical modifications on natural rubber.

David R. Burfield and coworkers [7], have studied the preparation methods and their effects on the various properties of modified rubber forms. Investigated Epoxidation routes include the use of bromohydrin intermediates, hydrogen-peroxide-catalyzed systems, and preformed peracetic acid. The latter reagent allows almost quantitative Epoxidation of natural rubber up to high modification levels with no detectable side reactions. The Kinetic reaction, thermal behavior, as well as physical properties were also investigated. Kinetic studies show that the peracetic acid Epoxidation is second order in peracid and rubber hydrocarbon with overall activation energy of 56.2 kJ/mol. It was also found that the Epoxidation leads to a progressive increase in Tg and polymer density with increase in modification level.

In another paper, **Chaiwat Ruksakulpiwat et al [8]** have reported the Synthesis and Modification of Epoxidized Natural Rubber from Natural Rubber Latex. The purpose of this research work is to modify natural rubber (NR). The optimum for synthesis of Epoxidized natural rubber (ENR) was investigated. The synthesized ENR was modified by hydrogenation reaction. This modified ENR was called hydrogenated Epoxidized Natural Rubber (HENR). The optimum amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ used in this reaction was investigated. It was found that the optimum condition for synthesizing ENR is as followed. The type of surfactant is POE (12) tridecyl ether and the amount of this surfactant is 5-part hundreds of rubbers (Phr). The highest epoxide content which received from fresh NR latex and concentrated NR latex in selected condition are 25.53 and 22.51% respectively. Thermogravimetric analyses (TGA) of ENR as well as modified ones were also studied. The highest percentage of hydrogenation from this condition is 67.90%. It can be concluded that after hydrogenation reaction HENR shows higher thermal resistance than that of synthesized ENR. The addition of hydrogen to the double bonds of natural rubber creates single bonds, resulting in a more stable and saturated polymer structure. This saturation limits the mobility of polymer chains and reduces the susceptibility to thermal oxidation and degradation reactions. The increased saturation also improves the resistance of the rubber to oxidative aging, thereby enhancing its thermal stability.

In another publication, **Narubeth Lorwanishpaisarn et al [9]** have studied the new approach to the Epoxidation of natural rubber through a sonochemical method. Epoxidized natural rubber (ENR) was synthesized using a sonochemical method. A coustic cavitation was employed for the Epoxidation reaction instead of heat and agitation. The effects of reaction time and temperature on the Epoxidation degree (EPD) were studied. The chemical structure

and EPD of ENR were assessed by Fourier transform infrared (FTIR) and proton nuclear magnetic resonance ($^1\text{H-NMR}$) techniques. At low reaction times (≤ 45 minutes), the EPD was independent of the reaction temperature but tended to increase with increasing reaction time. However, at sufficiently long reaction times (> 45 minutes), the EPD depended on both reaction time as well as reaction temperature, in other words, it increased slightly with an increase in reaction time up to 60 minutes before leveling off at the reaction temperatures of $20\text{ }^\circ\text{C}$ and $30\text{ }^\circ\text{C}$. However, at a higher reaction temperature ($40\text{ }^\circ\text{C}$), it tended to decline slowly with increasing reaction time, possibly due to the ring-opening reaction. The highest EPD, at approximately 30%, was achieved when synthesized by a sonochemical method at 30°C for 60 min, which is equivalent to that of the ENR synthesized by a conventional method at $60\text{ }^\circ\text{C}$ for 6 h. The properties of the raw ENR samples (with $\sim 30\%$ Epoxidation) prepared by different methods were also investigated. It was found that the ENR sample prepared by the sonochemical method possessed a slightly higher viscosity, initial plasticity number, and plasticity retention index than the ENR sample prepared by the conventional method. The results reveal the potential of the sonochemical method to supplant the conventional method for ENR synthesis, as it requires a considerably lower reaction temperature and time.

II.3 Cyclization of Natural Rubber

Cyclization of natural rubber refers to the process of forming cyclic structures within the polymer chains of natural rubber. Natural rubber, also known as polyisoprene, is a polymer made up of repeating isoprene units (C_5H_8).

The cyclization of natural rubber occurs through a chemical process called vulcanization or cross-linking. Vulcanization involves the addition of various chemicals, such as sulfur, accelerators, and activators, to the natural rubber compound. The process leads to the formation of covalent bonds between adjacent polymer chains, creating a three-dimensional network.

During vulcanization, sulfur atoms react with the double bonds present in the isoprene units of natural rubber. This reaction results in the formation of cross-links, where sulfur atoms bridge two polymer chains together. These cross-links create a network structure that imparts improved mechanical properties to the rubber, such as increased strength, elasticity, and resistance to heat, chemicals, and aging.

The cross-linking process can be controlled to achieve different degrees of cyclization, depending on the desired properties of the final rubber product. Higher levels of cross-linking

lead to a harder and less elastic material, while lower levels result in a softer and more flexible rubber.

Cyclization of natural rubber is a crucial step in the production of various rubber products, including tires, conveyor belts, seals, gaskets, and many other industrial and consumer goods. The vulcanization process enhances the durability and performance of natural rubber, making it suitable for a wide range of applications.

For example, **Mirzataheri et al [10]**, have studied the effect of cyclization of Natural Rubber on the physical and mechanical behavior. The effects of solvent, temperature, time, weight percent of catalyst on the rate and mechanism of cyclization of natural rubber (NR) was studied in toluene and xylene solutions having tin tetra chloride catalyst (SnCl_4). Iodometric titration show, with 8% SnCl_4 (based on polymer weight) cyclization occurs, leaving 27.4% of the total unsaturation. Infrared spectra of cyclized NR show decreased absorption intensity at 840 and 780 cm^{-1} which are characteristic bands of the linear polymer and the appearance of absorption band at 890 cm^{-1} as cycles were formed. By using this chemical modification, NR is transformed into a resinous thermoplastic, hard, non-rubbery cyclized material with much less unsaturation than the original rubber, which could find commercial applications as adhesives, printing inks, industrial and ship paints.

In another paper, **Sa-Ad Riyajan and coworkers [11]** have studied the Preparation of cyclized deproteinized natural rubber in latex state via a combination of benzotrichloride and sulfuric acid system, and its properties. Partially cyclized deproteinized natural rubber (DPNR) in latex form was successfully prepared by using a combination of sulfuric acid (H_2SO_4) and benzotrichloride (PhCCl_3) in the presence of Terric 320 as a non-ionic surfactant. The main parameters of the cyclization process such as various reaction times, dry rubber contents, concentrations of catalyst and temperatures were investigated. The resulting rubber was subjected to characterization by proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$), Fourier-Transform Infrared spectrometer (FTIR), Thermal Gravimetric Analysis (TGA), and Differential Scan Calorimeter (DSC). In addition, the topology of partially cyclized rubber was also analyzed by Transmittance Electron Microscopy (TEM). It was interesting to note that the obtained partially cyclized rubber using this catalyst system contained no gel, which was easily soluble in rubber solvents. They have also found that the T_g of cyclized DPNR increased with the increasing of degree of cyclization. The structure of cyclized rubber belonging to the aromatic ring of PhCCl_3 was measured by spectroscopic analyses. The TEM result indicates that the cyclization reaction should be occurred within the rubber particles

This is different from the partially cyclized rubber obtained from the other methods. Through, using structural characterization, it was found that the PhCCl_3 linked onto the rubber chain. It was also found that the thermal stability of this cyclized rubber was better compared to those of normal rubber. The efficiency of cyclization in this system could be increased by an increase of PhCCl_3 concentration.

II.4 Hydrogenation of Natural Rubber

Hydrogenation of natural rubber involves the chemical reaction of adding hydrogen (H_2) to the unsaturated bonds present in the polymer chains of natural rubber. This process is typically carried out in the presence of a catalyst, such as a transition metal catalyst, to facilitate the reaction.

The primary purpose of hydrogenation is to reduce or eliminate the double bonds in the natural rubber molecule. The unsaturated bonds in natural rubber are susceptible to oxidation and degradation, which can lead to reduced mechanical properties and increased vulnerability to aging. Hydrogenation helps to improve the stability, heat resistance, and durability of natural rubber.

The hydrogenation process involves the addition of hydrogen across the carbon-carbon double bonds, resulting in the conversion of these double bonds into single bonds. This reduces the overall degree of unsaturation in the polymer structure. The reaction is typically carried out at elevated temperatures and pressures to facilitate the hydrogenation reaction.

By hydrogenating natural rubber, several changes occur in the material's properties. The presence of double bonds contributes to the elasticity and tackiness of natural rubber. Hydrogenation reduces these properties, resulting in a material with improved heat resistance and reduced tackiness. The process also increases the resistance to oxidation and extends the overall lifespan of the rubber.

Hydrogenated natural rubber (**HNR**), often referred to as hydrogenated nitrile rubber (HNBR), finds applications in various industries, including automotive, aerospace, and oil and gas. It is used in the production of seals, gaskets, hoses, and other components where resistance to heat, chemicals, and aging is critical.

Overall, the hydrogenation of natural rubber modifies its molecular structure, reducing unsaturation and enhancing its properties especially the mechanical behaviour to meet specific applications requirements.

Nur Hanis Adila Azhar et al [12] have investigated the Hydrogenation of Liquid Natural Rubber Using Diimide. Liquid natural rubber (LNR) is a depolymerized natural rubber (NR) which consists of shorter polymeric chains and lower molecular weight ($M_w < 105$).

Hydrogenated LNR (HLNR) was synthesized via the thermal decomposition of p-toluene sulfonyl hydrazide (TSH) or 2,4,6-trimethylbenzenesulfonyl hydrazide (MSH). The LNR and HLNR structures were characterized by Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies. The thermal stability of hydrogenated Natural Rubber was also reported. The percentage of hydrogenation was calculated from NMR spectrum. The optimum percentage of hydrogenation (>90%) was achieved by manipulating the reaction parameters such as sources of di-imide, TSH concentration, solvent, and reaction time. The optimum condition was 3/1 weight ratio of TSH/LNR in o-xylene at 130°C in 4-hour reaction period. LNR's thermal stability had been proven to increase from 374°C to 462°C after 95.9% conversion of hydrogenation.

Suwadee Kongparakul et al [13] have reported the green Process for Natural Rubber Latex Hydrogenation via Metathesis. As we know, Natural rubber (NR) is an important renewable polymeric material which contains cis-1,4-polyisoprene as a major component. A new approach for a green hydrogenation process has been developed in their research work. From whom results, it can be clearly seen that this metathesis/hydrogenation method has less detrimental environmental impact and provides improved thermal stability of NR.

Non-catalytic Hydrogenation of Natural Rubber Latex was investigated and studied by **Mahittikul and coworkers [14]**. Hydrogenation is an important method of chemical modification, which improves the physical, chemical, mechanical, and thermal properties of diene-based elastomers. Natural rubber latex (NRL) could be hydrogenated to a strictly alternating ethylene-propylene copolymer using di-imide generated in an in-situ system. The di-imide generated using the in-situ technique for hydrogenation of NRL was accomplished by thermolysis of p-toluene sulfonyl hydrazide (TSH). A molar ratio of TSH to double bonds equal to 2: 1 was found to be the optimum ratio to provide a high percentage of hydrogenation. 95% Degree of saturation of NRL was achieved in o-xylene. Hydrogenated products are characterized by FTIR and NMR spectroscopy. The thermal stability of hydrogenated rubber was improved as shown from the results of Thermogravimetric analysis. From the differential scanning calorimetry measurement, the glass transition temperature of the hydrogenated product did appear to change. The di-imide hydrogenation method provides a viable process to improve the **thermal stability** of NRL with affecting its glass transition temperature. ($T_{g\ NR} = -64^\circ\text{C}$, $T_{g\ HNR} = -58^\circ\text{C}$).

II.5 Vulcanization of Natural Rubber

Vulcanization is a chemical process that is used to strengthen and improve the properties of natural rubber. It was discovered by Charles Goodyear in the mid-19th century and is still widely used today.

The vulcanization process involves the cross-linking of polymer chains in natural rubber using sulfur or other vulcanizing agents. When raw natural rubber is heated with sulfur and other additives, chemical reactions occur between the sulfur molecules and the polymer chains, forming cross-links or bridges between them. These cross-links give rubber its improved strength, elasticity, and resistance to wear, heat, and chemicals.

The vulcanization process typically involves the following steps:

1. **Mixing:** Natural rubber is first mixed with various compounding ingredients, such as sulfur, accelerators, activators, fillers, and antioxidants. This mixture is known as a rubber compound.
2. **Shaping:** The rubber compound is then shaped into the desired form, such as sheets or molded products.
3. **Heating:** The shaped rubber is subjected to heat, typically in the range of 140-180 degrees Celsius (284-356 degrees Fahrenheit), in the presence of sulfur. The exact temperature and time depend on the specific rubber compound and desired properties.
4. **Cross-linking:** During heating, the sulfur atoms react with the polymer chains, creating sulfur-sulfur bonds (known as "cross-links") between the chains. These cross-links effectively link the individual polymer chains together, forming a three-dimensional network structure.
5. **Curing:** After the cross-linking reaction is complete, the rubber is cooled and allowed to "cure" or "age" for a period of time. This allows the cross-links to stabilize and the rubber to reach its final properties.

The vulcanization process significantly improves the properties of natural rubber. It enhances its strength, durability, and resistance to abrasion, aging, and deformation. Vulcanized rubber also exhibits better elasticity and can withstand a wider range of temperatures compared to raw natural rubber.

Vulcanized rubber is commonly used in a wide range of applications, including tires, automotive parts, industrial products, footwear, gaskets, seals, hoses, and many other rubber-based products.

A.Pajarito [15] studied the vulcanization reaction by means of a Kinetic Model for curing agent systems which used for vulcanized rubber. Rheumatic properties of rubber compounds are usually monitored with time during the course of vulcanization at constant temperature. The measured vulcanization characteristics of rubber compound are used for quality control and evaluation of raw materials and product formulations. With the high number of ingredients used in typical formulations, it is important to identify ingredients which significantly affect the vulcanization characteristics of a rubber compound. His study reports the vulcanization characteristics of a natural rubber compound at 60 °C as function of ingredient loading. Rubber sheets are compounded according to a 212:8 fractional factorial design of experiment, where ingredients are treated as factors varied at low and high loadings. Vulcanization curves, which are time plots of elastic torque S' , viscous torque S'' , and $\tan \delta = S''/S'$, are measured for each rubber sheet using a moving die rheometer. The following responses are then determined from the vulcanization curves for data analysis: minimum elastic torque ML, maximum elastic torque MH, torque difference $\Delta S = MH - ML$, scorch time $ts1$, cure time $t'90$, cure rate index $CRI = 100/(t'90 - ts1)$, S'' and $\tan \delta$ values at ML and MH. Analysis of variance (ANOVA) shows used oil to be the main ingredient affecting vulcanization of the natural rubber compound (ML, MH, ΔS , $ts1$, S'' at ML and MH), followed by sulfur (MH, ΔS , CRI), calcium carbonate $CaCO_3$ (S'' at ML, $\tan \delta$ at MH) and diphenylguanidine DPG ($ts1$). High loading of used oil lowers the elastic and viscous response of the rubber compound, while increases the time for scorch. Increased loading of sulfur significantly enhances the elastic torque and cure rate of the compound. Ingredient loadings of used oil, sulfur, $CaCO_3$, and DPG affect the vulcanization characteristics of natural rubber compounds. At vulcanization temperature of 60°C, high loading of used oil decreases the elastic stiffness and increases the scorch safety time of rubber compounds. On the other hand, increased loading of sulfur vulcanizing agent enhances elastic stiffness but reduces the curing rate. High amount of accelerator DPG shortens the scorch safety time, while increased loading of $CaCO_3$ filler improves viscous stiffness. Used oil has the highest effect on vulcanization characteristics of studied rubber compounds, followed by sulfur, $CaCO_3$, and DPG.

In another paper, **Moez Kamoun et al [16]** have studied the Effect of Novel Binary Accelerator System on Properties of Vulcanized Natural Rubber. The mechanical properties, curing characteristics, and swelling behaviour of vulcanized natural rubber with a novel binary accelerator system were investigated. Their results indicate that the mechanical properties were improved. This could be attributed to the formation of tridimensional

structure between rubber molecular chains. Crosslinking density of vulcanized natural rubber was measured by equilibrium swelling method. As a result, the new binary accelerator was found to be able to improve both cure rate and crosslinking density. They have also found that the Effect was observed in the torque of the compound during vulcanization, because of the increased concentration of binary accelerator system, which creates an augmentation in modulus. Their results indicated also that the addition of the new binary accelerator was found to increase the rate of vulcanization significantly.

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Conclusion

Conclusion

Chemical modification of natural rubber can lead to various effects in its mechanical, thermal, physical, dynamic mechanical, and morphological properties such as:

1. Mechanical Properties: Chemical modifications can significantly affect the mechanical properties of natural rubber. Crosslinking and vulcanization increase the rubber's tensile strength, elongation at break, and tear resistance. These modifications make the rubber more durable and capable of withstanding mechanical stresses. On the other hand, excessive plasticization can reduce the rubber's mechanical strength but improve its flexibility and elongation.

2. Thermal Properties: Chemical modifications can enhance the thermal stability of natural rubber. Crosslinking and vulcanization increase the rubber's resistance to heat aging, preventing it from becoming brittle or degrading when exposed to high temperatures. These modifications also improve the rubber's dimensional stability, making it less prone to shrinking or deforming at elevated temperatures.

3. Physical Properties: Chemical modifications can alter various physical properties of natural rubber. Crosslinking and vulcanization increase the rubber's hardness, stiffness, and resistance to swelling by liquids or solvents. Plasticization, on the other hand, can soften the rubber and improve its processability. The addition of fillers or blending with other polymers can modify properties like density, electrical conductivity, and optical transparency.

4. Dynamic Mechanical Properties: Chemical modifications can affect the dynamic mechanical properties of natural rubber, which describe its response to dynamic forces or vibrations. Crosslinking and vulcanization improve the rubber's resilience, damping properties, and fatigue resistance. These modifications allow the rubber to absorb and dissipate energy more efficiently, making it suitable for applications that involve repetitive loading or vibration.

5. Morphological Properties: Chemical modifications can influence the morphological structure of natural rubber. Crosslinking and vulcanization promote the formation of a three-dimensional network of polymer chains, resulting in a more ordered and interconnected structure. This structural change enhances the rubber's mechanical properties and improves its

conclusion

resistance to deformation. Additionally, blending with other polymers or additives can alter the rubber's morphology, leading to changes in properties like porosity or surface texture.

It's important to note that the specific effects of chemical modifications on natural rubber will depend on factors such as the type and concentration of chemicals used, the reaction conditions, and the intended application of the modified rubber.

Abstract

Chemical modification of Natural Rubber involves the introduction of chemical groups or molecules into the polymer chain to enhance its physical, mechanical, and chemical properties. This review presents an overview of various methods of chemical modification, including grafting, Epoxidation, vulcanization, cyclization, and hydrogenation. Each method offers unique advantages in improving specific properties of Natural Rubber. Grafting functional groups onto the polymer chain enhances compatibility with other materials and improves mechanical properties. Epoxidation improves resistance to oxidation and enhances interfacial interactions. Vulcanization enhances mechanical strength and durability. Cyclization improves solubility and compatibility, while hydrogenation enhances heat resistance and stability. These chemical modifications broaden the range of applications for Natural Rubber in industries such as automotive, construction, and medical. This review highlights the significance of chemical modification in improving the properties and performance of Natural Rubber.

Keywords: Natural Rubber, Chemical modification, Epoxidation, Vulcanization, Cyclization, Hydrogenation, Physical, Mechanical, Chemical Properties.

Résumé

La modification chimique du caoutchouc naturel implique l'introduction des groupes chimiques ou des molécules dans la chaîne polymère afin d'améliorer ses propriétés physiques, mécaniques et chimiques. Cette revue présente un aperçu des différentes méthodes de modification chimique, notamment le greffage, l'époxydation, la vulcanisation, la cyclisation et l'hydrogénation. Chaque méthode offre des avantages uniques pour améliorer des propriétés spécifiques du caoutchouc naturel. Le greffage des groupes fonctionnels sur la chaîne polymère améliore la compatibilité avec d'autres matériaux et améliore aussi les propriétés mécaniques. L'Époxydation améliore la résistance à l'oxydation et renforce les interactions interfaciales. La vulcanisation d'un élastomère caoutchoutique améliore la résistance mécanique et la durabilité. La cyclisation améliore la solubilité et la compatibilité, tandis que l'hydrogénation renforce la résistance à la chaleur et augmente la stabilité thermique. Ces modifications chimiques élargissent le champ d'application du caoutchouc naturel dans des secteurs tels que l'automobile, la construction et le domaine médical. Cette revue met en évidence l'importance de la modification chimique dans l'amélioration des propriétés et des performances du caoutchouc naturel.

Mots-clés : Caoutchouc naturel, Modification chimique, Époxydation, Vulcanisation, Cyclisation, Hydrogénation, Propriétés physiques, Mécaniques, Chimiques.

ملخص

يتضمن التعديل الكيميائي للمطاط الطبيعي إدخال مجموعات كيميائية، مجموعات وظيفية أو جزيئات في سلسلة البولمر لتعزيز الخواص الفيزيائية والميكانيكية والكيميائية للمطاط الطبيعي. تقدم هذه المراجعة نظرة عامة على مختلف طرق التعديل الكيميائي، بما في ذلك التثبيت، والأكسدة، والفلكنة، والدوران، والتهجين. توفر كل طريقة مزايا فريدة في تحسين خصائص محددة للمطاط الطبيعي. يعزز تثبيت المجموعات الوظيفية على سلسلة البولمر التوافق مع مواد أخرى ويحسن الخواص الميكانيكية. تعزز الأكسدة مقاومة التآكسد ويعزز التفاعلات بين الواجهات. تعزز الفلكنة القوة الميكانيكية والمتانة. يحسن الدوران الذوبانية والتوافق، بينما يعزز التهجين مقاومة الحرارة والاستقرار. توسع هذه التعديلات الكيميائية نطاق التطبيقات للمطاط الطبيعي في صناعات مثل السيارات والبناء والطب. تسلط هذه المراجعة الضوء على أهمية التعديل الكيميائي في تحسين خصائص وأداء المطاط الطبيعي.

الكلمات المفتاحية: مطاط طبيعي، تعديل كيميائي، أكسدة، فلكنة، دوران، تهجين، خواص فيزيائية، خواص ميكانيكية، خواص كيميائية.