ADHESION PROPERTIES OF ULTRAVIOLET-CURED RUBBER BASED ADHESIVES BY BENZOYL PEROXIDE AS SOLE INITIATOR

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by

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LIST OF ABBREVIATIONS

ASTM	American Standard for Testing and Materials, USA	
CI	Coumarone-indene	
cm	Centimeter	
ENR	Epoxidized Natural Rubber	
g	Gram	
mm	Millimeter	
μm	Micron	
Ν	Newton	
N/m	Newton per meter	
N/m ²	Newton per area in meter	
NR	Natural Rubber	
SMR-L	Standard Malaysia Rubber (Type L)	
UV	Ultraviolet	

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Appendix ACharacterization and Adhesion Properties of UV-Cured Natural
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SIFAT PEREKATAN PEREKAT GETAH TERMATANG ULTRA LEMBAYUNG DENGAN MENGGUNAKAN BENZOIL PEROKSIDA SEBAGAI PEMULA TUNGGAL

ABSTRAK

Pemula UV secara biasa lebih mahal daripada pemula radikal bebas konvensional. Tambahan pula, dengan menggabungkan pemula UV dengan pemula radikal bebas konvensional boleh menyebabkan komplikasi inisiasi. Oleh itu, hal ini diperlukan untuk menilai pemula radikal bebas konvensional seperti benzoil peroksida sebagai pemula UV secara tunggal untuk memulakan pautan silang dalam perekat berasaskan getah dalam pematangan UV. Kajian ini penting kerana hal ini menunjukkan satu lagi ciri benzoil peroksida sebagai pemula UV secara tunggal berbanding dengan peranan benzoil peroksida sebagai pemangkin haba secara umumnya. Kajian ini akan menyumbang kepada kesusasteraan sedia ada dengan mengkaji sifat perekatan bagi perekat berasaskan getah di bawah pematangan sinar ultralembayung dengan menggunakan benzoil peroksida sebagai pemula UV secara tunggal. Parameter yang dianalisiskan adalah bilangan laluan UV (0, 5, 10, 15, 20), ketebalan salutan (60 µm dan 120 µm) dan jenis getah (SMR-L, ENR-25, ENR-50). Objektif pertama adalah untuk menilai kebolehan benzoil peroksida sebagai pemula UV secara tunggal untuk memulakan pautan silang dalam perekat berasaskan getah seperti yang dinilai oleh pengukuran kelikatan, ujian kandungan gel, FTIR dan kekerasan bandul. Berdasarkan keputusan tersebut, benzoil peroksida mampu digunakan sebagai pemula UV secara tunggal untuk memulakan pautan silang dalam perekat berasaskan getah. Kemudian, untuk objektif kedua, benzoil peroksida digunakan dalam rumusan untuk menyiasat kesan bilangan laluan UV, ketebalan

salutan dan jenis getah pada sifat kelekatan SMR-L, ENR-25 dan ENR-50. Bagi bilangan laluan UV, 15 laluan di bawah sinar ultralembayung merupakan bilangan optimum dalam skop penyelidikan ini. Disebabkan oleh bilangan oksiran yang optimum, perekat yang berasaskan ENR-25 menunjukkan kekuatan kupasan yang lebih baik berbanding dengan perekat yang berasaskan ENR-50 dan SMR-L. Disebabkan oleh fleksibiliti rantaian aliphatik panjang bertambahan dengan kesan penghabluran semula, perekat yang berasaskan SMR-L menunjukkan ketahanan dan kekuatan ricih yang lebih tinggi berbanding dengan perekat-perekat yang berasaskan ENR-25 dan ENR-50 Dalam kebanyakan ujian yang dijalankan, perekat yang lebih tebal berfungsi dengan lebih baik; sampel berlitupan 120 µm menunjukkan keputusan yang lebih baik daripada sampel berlitupan 60 µm disebabkan oleh peningkatan kuantiti untuk perekat akan meningkatkan sifat viskoelastik untuk perekat tersebut. Sampel berlitupan 120 µm menunjukkan kekuatan ricih yang lebih tinggi berbanding dengan sampel berlitupan 60 µm disebabkan oleh rintangan yang lebih tinggi terhadap tindakan ricih. Kesimpulannya, benzoil peroksida boleh digunakan sebagai pemula ultra lembayung untuk memulakan tindak balas paut silang pada perekat berasaskan getah dan sifat-sifat perekat yang dihasilkan pada sesetengah parameter yang dikaji adalah setara dengan perekat berasaskan getah yang dimatang secara haba. Aplikasi akhir kajian ini dijangka digunakan dalam industri pembungkusan.

ADHESION PROPERTIES OF ULTRAVIOLET-CURED RUBBER BASED ADHESIVES BY BENZOYL PEROXIDE AS SOLE INITIATOR

ABSTRACT

UV initiators are generally more expensive than conventional free radical initiator. Furthermore, combining UV initiator with conventional free radical initiator may induce initiation complication. Thus, there is a need to assess conventional free radical initiator such as benzoyl peroxide as sole UV-initiator to initiate crosslinking in UV-cured rubber-based adhesive. This study is significant since it addresses another characteristic of benzoyl peroxide as sole UV-initiator in contrast with its common role as thermal catalyst. This study will contribute to the existing literature by examining the adhesion properties of UV-cured rubber based adhesives by benzoyl peroxide as sole initiator. Parameters analysed were number of UV passes (0, 5, 10, 15, 20), coating thickness (60 µm and 120 µm) and type of rubber (SMR-L, ENR-25, ENR-50). The first objective is to assess the abilities of benzoyl peroxide as sole UVinitiator to initiate crosslinking in rubber-based adhesive as evaluated by viscosity measurement, gel content test, FTIR and pendulum hardness. From the results, benzoyl peroxide can be used as sole UV-initiator to initiate crosslinking in rubber-based adhesive. Then, in second objective, benzoyl peroxide was used in the formulation to investigate the effect of number of UV passes, coating thickness and type of rubber on the adhesion properties of SMR-L, ENR-25 and ENR-50. For the number of UV passes, 15 passes were the optimum number of passes under UV light within the scope of this research. Among most of the tests, thicker adhesives would perform better ;120 μ m coated samples showed higher performance than 60 μ m coated samples due to the higher amount of adhesive in the samples which improved the viscoelastic property of the adhesive. 120 μ m coated samples shown higher shear strength than 60 μ m coated samples due to the higher resistance to shearing action. Due to the optimum amount of oxirane rings, ENR-25 based adhesive demonstrated greater peel strength compared to ENR-50 and SMR-L based adhesives. Due to the flexibility of the former's long aliphatic chains and the strain recrystallization effect, SMR-L based adhesives had higher tackiness and shear resistance than ENR-25 and ENR-50 based adhesives. Overall, benzoyl peroxide can be used as sole UV-initiator to initiate crosslinking in rubber-based adhesive and the properties of the produced adhesive at some parameters are on par with thermal cured rubber-based adhesive. The end application of this study is expected to be used in packaging industries.

CHAPTER 1

INTRODUCTION

1.1 Overview

In rubber processing technology, the most important stage is crosslinking/vulcanization that confers mechanical and thermal stability to rubbers (Maria et al. 2016). Vulcanization is the process of chemically crosslinking rubber molecules with organic or inorganic substances under the influence of heat and pressure (Marković et al. 2020). Sulfur, as well as other non-sulfur vulcanizing agents like Sulfur Monochloride, Selenium, Nitrogen Sulfide (N₄S₄), benzoyl peroxide, etc., are the most often used vulcanizing agents (Sisanth et al. 2017). Photocuring is gradually being integrated into the natural rubber curing system in order to protect the environment and conserve energy (Xiang et al. 2019). Conventional natural rubber crosslinking are typically prepared by thermal curing (Boden et al. 2022). However, activators for the breakage of the sulfur ring (S_8) and accelerators for the creation of sulfur intermediates that aid in the facilitation of sulfur-to-double bond crosslinking are both required for the extremely complex reaction known as sulfur vulcanization (Kalyani Prusty 2019). Moreover, sulfur vulcanization is usually conducted at relatively high temperature in the range of 140-200 °C when compared to peroxide crosslinking and the require of activators in the accelerated sulfur curing method (Javier et al. 2022). In order to provide the necessary conditions for sulfur vulcanization, 100 parts of rubber are mixed with 5 to 8 parts of sulfur, and the mixture is heated for 3 to 4 hours at a temperature of about 141 °C (Gabriele Milani 2020). A higher temperature is needed to carry out the sulfur vulcanization process when compared to Benzoyl Peroxide crosslinking. On the other hand, when compared to a sulfur-vulcanized system, the networks contained more nonelastic defects (loops,

hanging chain ends), a heterogeneous crosslink distribution, and slower local segmental dynamics. (Howse et al. 2018) According to (D. Bornstein 2020), to cure rubbers for application usage that require fast curing rates, reversion resistance, superior heat aging, and better compression set, peroxide vulcanization could acts as crosslinking agent solely. Peroxide crosslinking is a relatively simple process when compared to sulfur vulcanization (Kruzelak et al. 2022). On the other hand, short crosslinking time, simple compounding, superior heat-aging resistance, reduced tension set and strain, no mold contamination, and the ability to create transparent rubbers are a few of the benefits of utilizing organic peroxides for crosslinking (Rostamitapehesmaeil 2023)

Radiation curing technology had gaining popularity in recent coatings technology. This technology can be exemplified by Ultraviolet (UV), Electron Beam (EB) and Gamma irradiations and is employed in many different applications (Jean-Pierre Fouassier 2021). However, UV and EB radiation curing are the most commonly used technology in recent technology. There are a few crucial factors to take into account while applying radiation curable coatings, such as the selection of the curing system. The choice is typically made based on elements including coating thickness, appearance, production rates, available space, and cost-benefit analysis (Wali et al. 2023). Radiation Curing is preferably compared to conventional thermal curing method due to the higher temperature and longer time for curing. In recent years, UV curing has gained more acceptance than EB curing. Rapid curing, a high rate of productivity, and low cost are the reasons for UV radiation curing to become a widely used method (Wali et al. 2023). Due to the combined attributes of rapid, energy-efficient curing at ambient temperature on radiation exposure and the potential to

achieve formulations devoid of volatile organic compounds, UV radiation curing is a well-established field of industrial relevance and research interest.

1.2 Problem Statement

UV initiated reaction normally requires a UV initiator or a combination of UV and conventional free radical initiator that normally used in thermal initiated reaction. The UV initiator absorb UV radiation to decompose to produce reactive species to directly start the reaction or transfer the reactive species to conventional free radical initiator to start the reaction. However, UV initiator are normally at higher cost than conventional free radical initiator, making a UV curable adhesive by using UV initiator not cost effective. Combination of UV initiator and conventional free radical initiator might complicate the initiation system. Thermal initiated reaction normally utilize higher temperature compared to UV initiator like benzoyl peroxide as sole initiator for UV curing rubber-based adhesives.

1.3 Objectives

- 1. To assess benzoyl peroxide abilities as sole UV-initiator in rubber-based adhesives on adhesion properties of SMR-L, ENR-25 and ENR-50.
- 2. To investigate the effect of number of UV passes, coating thickness, type of rubber on adhesion properties of SMR-L, ENR-25 and ENR-50.

1.4 Hypothesis

Hypothesis based on objective 1:

Based on UV absorbance range of Benzoyl Peroxide and UV light used and described in this thesis, it is hypothesized that benzoyl peroxide can be used as sole UV initiator for rubber based adhesive.

Hypothesis based on objective 2:

Factors analysed will resulted in different properties of adhesive.

1.5 Summary of All Chapters

In this thesis, there are 5 chapters included. In the first chapter, an introduction of study is given which covered the overview, problem statement and objectives. The literatures of studies such as natural rubbers, synthetic rubbers and UV curing adhesives are reviewed in detail. The description of the materials and sample preparation method and comprehensive information on how the research was performed is reviewed in Chapter 3. In Chapter 4, the results of study are shown which discussed according to the theoretical facts and compared with the previous studies. The conclusions and suggestions are summarized in the final chapter.

1.6 Scope of Study

The study described in this thesis investigated these parameters, number of UV passes (0, 5, 10, 15, 20), coating thickness (60 μ m and 120 μ m) and type of rubber (SMR-L, ENR-25, ENR-50) and assessed two objectives, ability of benzoyl peroxide as sole UV-initiator to initiate crosslinking in UV-cured rubber-based adhesives and how these parameters affect the adhesion properties of SMR-L, ENR-25 and ENR-50

rubber-based adhesives. This study will not cover initiation by connecting initiation by rubber-based adhesive.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Natural rubber is mostly composed of *cis*-polyisoprene, which may also contain small amounts of protein, dirt, and other contaminants from *Hevea brasiliensis* latex. Due to its renewability and environmental friendliness, natural rubber is commonly utilized in adhesives (A. et al. 2021). The dominant players in the current rubber industry, particularly for adhesive applications, are still synthetic rubbers. There are a wide variety of synthetic rubbers, including butyl rubber, nitrile rubber, polyisobutylene, and others, are widely utilized in this application (Khan and Poh 2011b). However, the widespread usage of synthetic rubbers raises environmental concerns and poses a risk to human health due to exposure to and inhalation of gases released by the rubbers (Nor and Ebdon 1998). Due to natural rubber itself with environmentally safe, non-toxic, and user-friendly qualities, it has attracted a lot of interest from the industry, particularly for adhesives applications. Natural rubber is renowned for having excellent adhesion properties, inherent of excellent elasticity and ability to crystallize under stretching (Hashim and Ong 2017).

Epoxidized Natural Rubber (ENR) is a type of modified rubber with characteristics more resembling in terms of properties to synthetic rubbers than to natural rubber (C.S.L. Baker et al. 1985; K.L. et al. 1983). As a form of natural rubber derivative, ENR has a variety of properties, including excellent damping, low gas permeability, strong wet grip, and oil resistance (Lee et al. 2010). Additionally, due to the ENR's distinctive structure, numerous chemical modifications by various functional groups and promising applications have been presented. Examples of these modifications and applications including vulcanized polymers, photo-crosslinkable rubbers, drug release polymers, antioxidant polymers, and flame-resistant polymers (D et al. 2001). Based on the origin of the raw materials and the more significant applications, the classification of adhesives are categorized as illustrated in **Table 2.1**.

Table 2.1 Classification of adhesives with relation to raw material origin and their more (Józef Kuczmaszewski 2006)

Item	Raw Material Base	More Important Applications
1	Epoxy Adhesives	For bonding metals, ceramics, glass,
		concrete, wood, rubber, polymer
		plastics, also for renovation, casting
2	Adhesives based on natural	For bonding rubber, leather, felt,
	rubber	textiles

However, due to the natural rubber is brittle at low temperatures and is soft at high temperatures before crosslinking occurs, it exhibits low mechanical and thermal hardness, the most crucial aspect of the adhesive characteristics is the curing process. Rubber chains are crosslinked to prevent them from sliding and entangling with one another when under load (Sperling 2005; Thomas et al. 2013). High reversible deformability, strong mechanical strength, elasticity, and thermal hardness are all characteristics of crosslinked natural rubber (Kim et al. 2020). According to (Kim et al. 2020), the crosslink reactions are crucial for enhancing rubber's general performance.

Photocuring is gradually integrated into the natural rubber curing system in order to protect the environment and conserve energy. Conventional natural rubber crosslinking are typically prepared by thermal curing. Activators for the breakage of the sulfur ring (S_8) and accelerators for the formation of sulfur intermediates that aid in the facilitation of sulfur-to-double bond crosslinking are both required for the extremely complex reaction known as sulfur vulcanization (Mohammad and Simon 2006). Moreover, sulfur vulcanization is usually conducted at relatively high temperature in the range of 140-200 °C when compared to peroxide crosslinking and the require of activators in the accelerated sulfur curing method (Mohammad and Simon 2006). On the other hand, compared to a sulfur-vulcanized system, the networks had more nonelastic defects (loops, hanging chain ends), a heterogeneous crosslink distribution, and slower local segmental dynamics (Howse et al. 2018). According to (D. Bornstein 2020), to cure rubbers for application usage that require fast curing rates, reversion resistance, superior heat aging, and better compression set, peroxide vulcanization can operate as a crosslinking agent solely. Due to the unique curing mechanism, which includes handling flexibility, enhanced resin stability, rapid curing speed, energy deficiency, etc., radiation curing, especially UV radiation curing, offers some distinct technological superiority compared to thermal curing. Furthermore, compared to the thermal curing procedure, there is also a lot of control and some process latitude to create complicated and substantial structures (Abliz et al. 2013). However, in terms of free radical initiators in UV radiation curing, there are 3 main types namely azo, peroxide and redox type initiators. They are commonly used as initiators in UV radiation curing.

2.2 Rubber As Primary Resin

2.2.1 Standard Malaysian Rubber (SMR)

SMR (Standard Malaysian Rubber) natural rubbers are rated based on technical criteria rather than the conventional visual standards. Due to the cure rate and possessability can differ, the standardization of the smoked sheet and pale crepe from different plantations is necessary. A paradigm shift in the way natural rubber is produced and marketed occurred with the introduction of the Standard Malaysian Rubber (SMR) Scheme in 1965. An international scheme for Technically Specified Rubber (TSR) has adopted this scheme due to it was so successful. These compact, compacted bales or sheets of Technically Specified Rubber (TSR) are available. These schemes encouraged the use of fewer grades, all with established quality criteria, and packaged in manageable compact polyethylene-wrapped bales (33.3 kg) for factory handling, shipping, and storage. The manufacturing of TSR is distinct from conventional rubber production. An illustration of the SMR scheme with the relationship between source materials and grade is shown in **Figure 2.1** (Fulton et al. 1982).

Grades of Standard Malaysian Rubber



Figure 2.1 Processing routes using raw materials to create the various grades of Standard Malaysian Rubber (Fulton et al. 1982)

The natural rubber is graded by SMR, and other nations, such SLR from Sri Lanka, SIR from Indonesia, TTR from Thailand, etc., are graded as a result of the natural rubber's marketing accomplishments (Hofmann 1989). The SMR-L production is focused on its color. The light-colored SMR is produced by adding sodium metabisulfite at a dry rubber content (DRC) of 0.04%. **Table 2.2** shows the SMR-L properties and specifications (Fulton et al. 1982) **Figure 2.2 and 2.3** show the structures of SMR-L and cis-1,4-Polyisoproprene of SMR-L (Fulton et al. 1982).

Parameters	Value
Dirt retained on 44µ aperture (max), % wt	0.02
Ash content (max), % wt	0.50
Nitrogen (max), % wt	0.60
Volatile matter (max), % wt	0.80
Wallace rapid plasticity (Po), min	30
Plasticity Retention Index (PRI), min, % ^b	60
Lovibond color:	
Individual value (max)	6.0
Individual range (max)	2.0

Table 2.2 SMR-L properties and specifications (Fulton et al. 1982)

^bSpecial producer limits and related controls are also imposed by RRIM to provide

safeguard



Figure 2.2 Structure of SMR-L (Fulton et al. 1982)



cis-1,4-Polyisoprene (SMR L)

Figure 2.3 Structure of cis-1,4-Polyisoproprene of SMR-L (Fulton et al. 1982)

2.2.2 Epoxidized Natural Rubber (ENR)

Epoxidized Natural Rubber (ENR) is considered as a modified natural rubber (NR) (Baker and Gelling 1987). **Figure 2.4(a)** depicts a typical formation of ENR using peracetic acid from NR, cis-1, 4-isoprene. (Baker and Gelling 1987) Isoprene (C) and epoxidized isoprene (E) serve as monomer units that are randomly distributed throughout the polymer chain (P.C. 1987). There are commercially available products for different degrees of NR epoxidation. For example, the polymer chain's isoprene units are 25%, 50%, and 75% epoxidized in ENR-25, ENR-50, and ENR-75, respectively. **Figure 2.4(b)**depicts the general structure of ENR-50 and the arrangement of the carbon atoms for nomenclature purposes.



Figure 2.4 (a) ENR modification from NR and (b) the general structure and the arrangement of carbon atom in ENR-50 employed in this work (Baker and Gelling 1987)

Epoxidized natural rubber (ENR), which is established by chemically modification of natural rubber, is now a well-known commercial product. There are two grades available with epoxide contents of 25 and 50 mole%. They possess a unique set of characteristics that provide high strength, including the capacity to experience strain crystallization and higher glass transition temperatures and solubility parameters. These characteristics are reflected in vulcanizates with improved adhesive properties, lower gas permeability, higher damping, and increased oil resistance. Without the need for coupling agents with particular interactions via epoxide groups, it produced a high degree of reinforcement with silica fillers. ENR forming compatible blends with a range of chlorine-containing polymers also resulted functional group interactions. The reactions between the epoxide groups in ENR and reactive groups on other polymers result in 'self-vulcanising' blends. There are practical formulations and number of applications, including tyres, are outlined.

Although the product's structure was not clarified, natural rubber (NR) and peroxyacid were reacted, and epoxidation must have taken place as early as 1922 (P.A. 1922). Since then, a number of contradictory reports regarding the preparation and

characteristics of epoxidized natural rubber (ENR) have been published. Numerous reaction conditions were used, and the results were differently described as being either hard thermoplastic or soft rubbery polymers (Appl. 1965; D. et al. 1984; E.H. 1934; J.F. et al. 1979; L.J. et al. 1981; Patent 1932).

Due to the oil crises, there was a resurgence of interest in natural rubber chemical modification to create various polymeric materials in the early to mid-1970s. There were a number of factors that made epoxidation appealing. Epoxidation is a simple reaction process that may be carried out in the latex phase. Additionally, the reagents needed for the reaction are generally low cost (Baker and Gelling 1985).

2.2.3 Preparation and Structure of Epoxidized Natural Rubber

The chemistry of epoxidation of unsaturated low molecular weight compounds is well established (C. Barlow 1978; D. 1971; N.S. et al. 1959) and it is known that secondary ring-opened reactions of the initially formed epoxide group can occur (N.S. et al. 1959). A systematic study revealed that the generation of secondary ring-opened products was favoured by high total acid concentrations and high temperatures (A.D. n.d.; J.F. et al. 1979; M. et al. 1988). Two different forms of ring-opened products are available, principally depending on the degree of epoxidation. The dominant ringopened products are those anticipated from simple epoxide chemistry, and the majority of epoxide groups are separated at low levels of modification (A. 1964)(**Figure 2.5**). The *trans* diol is typically the final product, but dehydration of the tertiary alcohol may happen. As the degree of modification is increased, the number of adjacent epoxide groups increases and a five-membered cyclic ether becomes the major product (Gelling 1985; J.F. et al. 1979). This happens when an epoxide with its ring opened attacks the nearby epoxide group. The reaction then continues up the rubber backbone until it is halted by another epoxide group or steric constraints (**Figure 2.6**). The various ringopened structures were characterized by a combination of IR and HNMR spectroscopy and by model chemistry (Gelling 1985; J.F. et al. 1979). As illustrated in **Figure 2.6**, The formation of ether crosslinks is responsible for the fact that most epoxidation products with ring-opened structures are insoluble, as shown by the acid catalyzed ringopening of epoxides model. Gan et al (L.J. et al. 1981) observed ring-opened structures as reported above in the epoxidation of NR latex with formic acid and hydrogen peroxide.



Figure 2.5 Epoxidation of NR with a peroxyacid and secondary ring-opening of isolated epoxide groups (L.J. et al. 1981)

During the epoxidation of NR, in the light of the established ring-opening chemistry that can occur, it is easy to understand the variety of products that were reported in the earlier literature on this topic. NR can be epoxidized to 100% under favorable ring-opening conditions, producing a tough thermoplastic material known as furanised NR (I, Scheme 2). Many of this material's characteristics are similar to those of polystyrene. (I.R. 1985).



Figure 2.6 Ring-Opening of Adjacent Epoxide Groups to Yield Five-Membered Cyclic Ethers (I.R. 1985)



Figure 2.7 Crosslinking of ENR via ring-opened epoxide groups (I.R. 1985)

Under strictly controlled conditions, NR latex can be epoxidized to above 75% mole without the formation of secondary ring-opened structures. Both the '*in-situ*' generation of peroxyformic acid (British Patent 2, 113 1982) or the preformed peroxyacetic acid (C.S.L. et al. 1985; J.F. et al. 1979) from formic acid and hydrogen peroxide can be employed (**Figure 2.8**). Due to the consumption of only hydrogen peroxide, the latter method is chosen for commercial production.

$$H_2O_2 + HCOOH \implies HCOOOH + H_2O$$



Figure 2.8 The in-situ epoxidation of NR employing formic acid and hydrogen peroxide (S.C. et al. 1986)

Peroxyacetic acid epoxidation of NR is a second order reaction with an overall activation energy of 52.6kJ/mol (D. et al. 1984; T. et al. 1976). A significant factor affecting the *in-situ* epoxidation rate is the synthesis of peroxy formic acid from formic acid and hydrogen peroxide. (S.C. et al. 1986). The double bond concentration changed in the hydrocarbon phase also effects reaction rates which has been shown in a more detailed study (D.S. 2018). Although reaction conditions have been established which yield ENR free from secondary reaction products, ¹H NMR spectra of these materials (**Figure 2.9**) do not reveal any information on their structure.

Latex epoxidations are two phase systems and this heterogeneity could control the product structure. If the rate of epoxidation is greater than the rate of diffusion of the peroxycarboxylic acid into the particle since NR latex particles vary in size from $0.02 \,\mu\text{m}$ to over 2.0 μm then a heterogeneously epoxidized product would be expected.



Figure 2.9 ¹H NMR spectrum of 50 mole% Epoxidized Natural Rubber (J. 1956)

The outer shell of the latex particle would be epoxidized to 100% while the interior would be unmodified at an epoxidation level of 50 mole% in the extreme case. The mathematics of diffusion of a substance through a medium with which it can simultaneously react are well established (J. 1956). Diffusion is not the controlling factor indicated by the calculations based on approximate diffusion coefficients and epoxidation rates. This is supposed by size partitioning of NR latex followed by epoxidation; there were no differences in rate or epoxidation level observed (D.S. Campbell 1985). Further confirmation is obtained from ¹³C NMR. The mole% of the variously positioned epoxide groups can be calculated for any level of epoxidation if it is assumed that the epoxidation of unsaturated units is random (**Figure 2.9**).

2.3 Adhesive Main Constituents

2.3.1 Primary Resins

Rosin is one of the oldest raw materials in the manufacturing of rubber adhesives. In America's first large-scale industry, gum rosin extraction from living pines was initiated in the year 1606. Rosin resins can be obtained from three types of rosin such as wood, gum and tall oil. Rosin ranges in color from yellow to black and is semitransparent (Austin 1984; Mitchell et al. 2016). There are different types of resins used in rubber industry namely, Coumarone-indene resins, petroleum resins, terpene resins, vegetable resins, natural rosins, and etc. In this research, coumarone-indene resins was chosen due to it is commercially available.

2.3.2 Tackifier

Coumarone-Indene (CI) resin ($C_{17}H_{14}O$) was firstly manufactured commercially as a substitute material in the United States in 1950. The rapid acceptance and expansion of coumarone-indene resins brought an increase in demand for coumarone-indene resins. Production of coumarone-indene resins has been gradually increasing recently, and they can be utilized for a variety of purposes, including coatings, inks, rubber adhesives, and other things (Henglein 2013; Zohuriaan-Mehr et al. 2000). Coumaroneindene resins are typically thermoplastic blends of polycoumarone and polyindene. They are created through the polymerization of coumarone with indene (Board 2007). Under the influence of light, catalyst, or heat, polymerization occurs. Due to the existence of the double bond in the side chain, which is owned by the Allyl group, Coumarone-Indene resin is responsible for having free double bonds in polymeric chain structures. This results in good Green Tack to the rubber compounds. It will also heal this double bond during the vulcanization process. Depending on the ratio of coumarone to indene in the coumarone-indene resin, a wide range of grades with melting points between 60°C and 140°C and colors ranging from bright yellow to dark brown can be generated. Additionally, CI resins are soluble in ketones, hydrocarbons, and esters and have strong electrical insulation properties in addition to being chemically inert.

The excellent tackifier and processing aid of CI resin which is utilized in the compounding variety of rubbers such as NBR, EPDM, CSM, CPE, NR, ACRYLIC RUBBERS, and MILLABLE PU. When mixing rubber compounds in two-roll mills, Kneader, or Banburry, CI resin is added at the beginning of the cycle of mixing; however, it can be employed in conjunction with the addition of fillers. Additionally, it serves as a tackifier in rubber-based contact adhesives. Tackifier resin is typically applied to an adhesive to improve its tack properties. This research utilized coumarone-indene (CI) resin as a tackifier. Some of these resin's characteristics include its bulk form, lack of smell, and dark brown color. It is obtained from the coal naphtha fraction and is typically not separated with the indene that occurs with it. By heating coumarone and indene with sulphuric acid at 0°C in the presence of catalyst, this thermosetting resin is created and induced polymerization, as shown in **Figure 2.10**. In the production of rubber-based adhesive, it acts as a tackifier (Alger 1989).

Figure 2.10 Chemical reaction of coumarone-indene resin polymerization (Alger 1989)

2.3.3 Solvent

Toluene, also known as toluol, is a water-insoluble liquid that is clear and colorless and has the similar smell of paint thinners. Toluol is the name for tolu balsam, an aromatic extract that was originally obtained from the tropical American tree Myroxylonbalsamum. The name was originally given by Jöns Jakob Berzelius. The IUPAC designation for toluene is methylbenzene. It is an aromatic hydrocarbon that is frequently employed as a solvent. Toluene is a typical solvent that may dissolve a variety of substances, including paints, various chemical reactants, paint thinners, rubber, printing ink, adhesives, lacquers, leather, tanners, disinfectants, and glues. Toluene also reacts towards electrophilic aromatic substitution as a normal aromatic hydrocarbon (Greenberg et al. 1985).

Figure 2.11 Chemical Structure of Toluene (Greenberg et al. 1985)

According to (Greenberg et al. 1985), there are currently no known health or environmental risks associated with toluene exposure in the general population or environment, according to the available data. Toluene can be considered as the technological product whose main ingredient is typically generated from petroleum fractions comprising catalytically dehydrogenated methylcyclohexane. Purification of toluene products involves azeotropic distillation using paraffinic hydrocarbons, naphthenic hydrocarbons, or alcohols. Due to the numerous processes used to generate toluene, the range of impurities varies greatly. Technical grades of toluene contain benzene as a significant common contaminant, but highly-purified toluene (reagent grade and nitration grade) contains less than 0.01% benzene (Greenberg et al. 1985). In this research, the toluene used contains with 0.005% benzene.

However, benzene is the only one of the four chemicals that has been proven to be a human carcinogen, according to a risk assessment conducted by (Masilu Daniel Masekameni, Raeesa Moolla, Mary Gulumian 2019) to characterize the emissions of volatile organic compounds (VOCs) for benzene, toluene, ethylbenzene, and xylenes (BTEX). However, benzene is the least quantifiable VOC, but given its danger to human health, it is concerning based on the proportion contribution of each BTEX pollutant. When compared to the other four pollutants, toluene was determined to contribute the least to VOCs (BTEX). Toluene was chosen and used in this research as the solvent for all of the samples in the experiment because it is a commercially available product (Poh et al. 2008).

2.4 Crosslinking of Rubber

2.4.1 Compounds for Crosslinking Process

2.4.1(a) Sulfur Vulcanization

Historically, the phrase "vulcanization" referred to the heating of rubber, sulfur, and white lead (Tobolsky and Eisenberg 1959). By nomenclature, vulcanization refers to the crosslinking process for rubber that uses sulfur or sulfur compounds. Moreover, the phrase "hardening" or "curing" in the rubber business typically refers to crosslinking based on the rubbers' reaction with a substance other than sulfur, while the terms "sulfur cure" and "sulfur vulcanization" are often used interchangeably (Tobolsky and Eisenberg 1959). Vulcanizate is the term refers to the rubber which is chemically crosslinked (A.Y. Coran 2014). In rubber chemistry, the general term is considered as crosslinking. In this research, crosslinking is used as a more general term. **Figure 2.12** shows the formation of a crosslinked molecular network (A.Y. Coran 2014). One of the most vital compounds in vulcanization is the crosslinking agent. The most popular crosslinking agent in the rubber industry is elemental sulfur (A.Y. Coran 2014). During this complex and intricate process, sulfur-based connections (monosulfidic, disulfidic, and polysulfidic) are formed between rubber chain segments (Mansilla et al. 2017).