STUDY OF ADHESION PROPERTIES OF NATURAL RUBBER, EPOXIDIZED NATURAL RUBBER, AND ETHYLENE-PROPYLENE DIENE TERPOLYMER-BASED ADHESIVES

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2007

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by

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**Thesis submitted in fulfilment of the requirements
for the Degree of
Master of Science**

January 2007

ACKNOWLEDGEMENTS

Heartiest thankful goes to Assoc. Prof. Dr. Poh Beng Teik since he agreed to become my very Supervisor for the lab work and tried to assist me in filling forms for pursuing the Degree of Master of Science. He had been providing me a lot of opportunities and flexibilities in viewing out my own ideas and most of them were supported by him. The guide that had given by him was remarkably useful and really helpful. He was never being selfish to view out his opinions for my guidance and he is definitely a sincere person.

The fully spiritually support, love and care, and partially financial that had given by my family is gratefully acknowledged. The author has no reason for not to express his sincere gratitude to his parents for their encouragement between the course of this research and until the writing of this thesis.

Lastly, the author shall thank Universiti Sains Malaysia (USM) for its wonderful study environment and beautiful landscape. Special thankful makes for Institute of Graduate Studies (IPS) and personnel for making this study possible through a postgraduate assistantship. The author at very last not forget to express his very last thankful to School of Industrial Technology, USM for providing him facilities and very much opportunities to work and co-operate with all staffs and lecturers.

Thank you to you all for everything. May God bless you.

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LIST OF ABBREVIATIONS/SYMBOLS

ASTM	=	American Standard for Testing and Materials, USA
b.p.	=	Boiling point
BrENR	=	Brominated epoxidized natural rubber
BrNR	=	Brominated natural rubber
CI	=	Coumarone-indene
ClENR	=	Chlorinated epoxidized natural rubber
ClNR	=	Chlorinated natural rubber
cm	=	Centimetre
cP	=	Centipoises
CR	=	Chlorinated rubber
3-D	=	Three-dimensional
ENR	=	Epoxidized natural rubber
EPDM (EPT)	=	Ethylene-propylene diene terpolymer
EVA	=	Ethylene-vinyl-acetate
g	=	Gram
GP	=	Gutta-percha
h	=	Hour
HENR	=	Hydrogenated epoxidized natural rubber
lb	=	Pound
lb_f	=	Pound feet
lb_f/ln^2	=	Pound feet per square inch
kg	=	Kilogram
KJ	=	Kilo joule
kN/m	=	Kilo Newton per metre
μm	=	Micron
mm	=	Millimetre
mm/min	=	Millimetre per minute
mm/s	=	Millimetre per second
M_n	=	Number-average molecular weight
m.p.	=	Melting point
MPa	=	Megapascal
M_w	=	Molecular weight
N	=	Newton
NBR	=	Nitrile-butadiene rubber
NMR	=	Nuclear magnetic resonance
NR	=	Natural rubber
PF	=	Phenol formaldehyde
phr	=	Parts per hundred parts
PSA	=	Pressure sensitive adhesive
PVC	=	Poly(vinyl chloride)
r	=	radius
RH	=	Relative humidity
rpm	=	Rotation per minute
RRIM	=	Rubber Research Institute of Malaysia
SAN	=	Styrene-acrylonitrile
SBR	=	Styrene-butadiene rubber
SBS	=	Styrene-butadiene-styrene
S.D.	=	Specific density
S.G.	=	Specific gravity
SIS	=	Styrene-isoprene-styrene
SMR	=	Standard Malaysian Rubber

SMR 5	=	Standard Malaysian Rubber (Impurities ≤ 0.05 %)
SMR 5CV	=	Standard Malaysian Rubber Constant Viscosity (Mooney 60 ± 5)
SMR EQ	=	Standard Malaysian Rubber Extra Quality
SMR GP	=	Standard Malaysian Rubber General Purpose
SMR L	=	Standard Malaysian Rubber (Like SMR 5 but lighter colour)
SMR 5LV	=	Standard Malaysian Rubber Low Viscosity (Mooney 50 ± 5)
SOP	=	Standard Operation Procedure
s.p.	=	Softening point
Syn.	=	Synonym
TPE	=	Thermoplastic elastomer
T_r	=	Room temperature
UV	=	Ultraviolet
VOCs	=	Volatile organic contents
θ	=	Contact angle
α	=	Cone-plate angle

Kajian Mengenai Sifat-sifat Perekatan pada Perekat yang Berasaskan Getah Asli, Getah Asli Terepoksida, dan Etilena-Propilena Diena Terpolimer

ABSTRAK

Kekuatan kupasan, ketahanan ricihan dan sifat-sifat lekitan pada perekat yang berasaskan getah asli terepoksida (ENR), getah asli (SMR) dan getah sintetik, EPDM telah dipelajari dan dikaji. ENR terbahagi kepada dua gred, iaitu ENR 25 and ENR 50, di mana masing-masing mengandungi 25 dan 50 mol % kumpulan epoksi. Sebanyak tiga gred SMR, iaitu SMR L, SMR 10 dan SMR 20, yang berbeza dari segi kandungan kotoran khususnya, telah dipelopori dan dikaji. Sumber getah ini telah dikenakan mastikasi dalam empat jangka masa yang berlainan bagi mempelbagaikan struktur panjang rantai getah. Resin coumarone-indene (CI) telah dipilih sebagai pelekit dalam keseluruhan kajian. Selain itu, petroresin dan gum rosin telah juga digunakan secara berasingan tetapi dalam keadaan terpilih. Kandungan pelekit berbeza dari 0 hingga 80 phr (bahagian per seratus bahagian getah). Pelarut toluena digunakan untuk meleraikan getah kepada suatu larutan supaya dapat memudahkan lagi pengujian ke atasnya. Perekat ini kemudian disapukan ke atas substrat dengan menggunakan SHEEN hand-coater. Setiap sampel disapukan mengikut empat ketebalan permukaan, iaitu 30, 60, 90, dan 120 μm. Kekuatan kupasan sampel perekat getah ditentukan oleh alat penguji perekatan Lloyd melalui tiga mod ujian (T-Peel Test, 90° Peel Test, 180° Peel Test), dengan berpandukan piawaian daripada ASTM. Mesin ini juga dipakai gunakan untuk Loop Tack Test manakala dua ujian lekitan lain adalah menerusi Ball Rolling Tack Test dan penentuan likatan. Shear Resistance Test dilakukan dengan menggunakan Texture Analyser. Daripada keputusan ujian, kekuatan kupasan tertinggi telah ditunjukkan pada setiap perekat yang berasaskan getah pada ketebalan 120 μm, manakala terendah pada sampel yang berketebalan 30 μm. Dalam setiap ketebalan ini, diperhatikan satu titik maksimum pada 40 phr resin CI. Jelasnya,

perekat berasaskan ENR 25 telah menunjukkan kekuatan kupasan dan ketahanan ricihan yang lebih tinggi berbanding perekat berasaskan ENR 50 dan getah lain. Sebaliknya, perekat berasaskan EPDM, diikuti SMR L telah memberikan sifat-sifat lekitan yang lebih baik berbanding SMR lain manakala getah berasaskan ENR 50 dan ENR 25 adalah kurang memuaskan. Pengaruh masa mastikasi ke atas kekuatan kupasan, ketahanan ricihan dan sifat-sifat lekitan pada perekat juga dikaji dan dibincangkan.

Study of Adhesion Properties of Natural Rubber, Epoxidized Natural Rubber, and Ethylene-Propylene Diene Terpolymer-Based Adhesives

ABSTRACT

The peel strength, shear resistance and tackiness properties of epoxidized natural rubber (ENR), Standard Malaysian Rubber (SMR), and ethylene-propylene diene terpolymer (EPDM)-based adhesives were studied. Two grades of ENRs, i.e. ENR 25 and ENR 50 having 25 and 50 mole % epoxidation were respectively used as the elastomers. Whereas as many as three grades of SMRs, viz. SMR L, SMR 10 and SMR 20 varying from their dirt content and other foreign substances were studied. These rubbers were masticated at different mastication times in order to vary the rubber chain lengths. Coumarone-indene (CI) resin had been chosen as tackifier throughout the study. As comparison, there is presented two other resins in the selective conditions, and they were petroresin and gum rosin. The concentration of tackifier ranged from 0 to 80 phr (parts per hundred parts of rubber). Toluene was used as the solvent to prepare the adhesives into solution for testing. Coating on substrates was carried out using a standard SHEEN hand-coater. For each adhesive sample, four levels of coating thicknesses were carried out, i.e. 30, 60, 90, and 120 μm. Peel strength of the adhesives was determined by the Lloyd adhesion tester instrument using three different testing modes (T-Peel Test, 90° Peel Test, 180° Peel Test) in accordance with ASTM specifications. The machine was also used for Loop Tack Test whilst two other tackiness tests were via Ball Rolling Tack Test and viscosity measurement. Another test, named Shear Resistance Test was carried out by means of Texture Analyser. Results indicated that for all rubber-based adhesives, 120 μm coated sample showed the highest peel strength whereas the lowest peel strength was exhibited by 30 μm coated sample. For a fixed thickness of coating, the maximum peel strength occurred at 40 phr of coumarone-indene resin. Obviously, ENR 25-based

adhesive showed a better peel strength and shear resistance compared to that of ENR 50, and other rubber-based adhesives. Reversely, EPDM and SMR L-based adhesives indicated higher tackiness than those from other SMRs-based adhesives whilst ENR 50 and ENR 25-based adhesives were the lowest. The effect of mastication time on peel strength, shear resistance and tackiness property of the adhesives were also studied and discussed.

CHAPTER 1 – INTRODUCTION

General

The adhesion properties of natural rubber (NR) and epoxidized natural rubber (ENR) were much discussed in this thesis.   Discussion is ranged from the historical background of these rubbers, followed by objective of the rubber research, etc., until the future prospects in rubber technology.

NR here refers to Standard Malaysian Rubber (SMR).   It is sticky, coloured, produced in large size varying in kilograms (kg).   Because of the nature of SMR, a great potential for various applications may have derived since more than four decades ago.   Rubber Research Institute of Malaysia (RRIM) has very much concentrated on the quality assurance of the production of rubbers in order to produce as lowest dirt content as possible by means of manufacturer's instruments and technologies.   SMR is well-known and recognized throughout the world, especially by developing industrialized countries like United States of America, European Union (EU), Japan, Korea, etc. because of its cost effectiveness, usable, harmless especially to one's health.

ENR is more or less popular due to two grades of ENRs, viz. ENR 25 and ENR 50. These ENRs are chosen as their moderate cost, great adhesion properties, and easily gained by means of the production line via a simple and quite rapid route using peroxy acid onto NR.   A slightly changes in chemical structure in the presence of oxiranes making possible for ENR to possess other properties such as heat resistance, air permeability resistance, and stability due to chain re-arrangement.

The only synthetic rubber, ethylene-propylene diene terpolymer (EPDM) was used for comparison with those of ENRs and SMRs. EPDM is essentially a transparent, non-tacky, difficult-to-masticate material. EPDM has been largely applied for roofing and tyres production. Tyre for example, is highly resisted to abrasion at either very high or low temperature on the road. Recompounding EPDM and reinforcing have very much studied for improved tack and adhesion for both roofing and tyres use (Morton, 1987a; Crowther and Melley, 1974). However, is that possible for EPDM to shift to adhesive level in the future? Yes, it could be, by addition of certain resin, filler, or accelerator, an EPDM-based adhesive could be prepared and it is possibly used in tape or label.

All these rubbers made in rubber-based adhesives, separately. A series of testing had been carried out, of which ranged from Peel Test, Shear Resistance Test to Tackiness Test, to determine the tack and adhesion properties. Different test mode will probably be varying the final average value of tackiness and adhesion strength owing to different evaluation formula. In accordance with ASTM Standard, each adhesion test should have its own preparation and operation ways. They differ from each other. Tests are carried out carefully and separately for each sample, without rush. Data collecting is an important task as there might be occurred data mixing and this should be avoided.

Moreover, one should be able to carry out a test systematically, for instance one sample followed by one sample but not mixing the samples from different formulations. Smart time management is as important as other parts in experimental as a little mistake may cause serious implication at the end. One may have to repeat again overall experiment from the beginning. For example, one supposes to measure viscosity for all adhesive samples on Friday, but he forgets or careless not to do so. The related adhesive in the beaker is left for another two days before measuring on next

Monday.   The viscosity of the sample could possibly be different within two days.   A repetition needs time and energy as well as cost but nothing one could do unless he or she can manage time wisely.

Furthermore, lab work could be divided into preparation of material and testing of sample, two major tasks.   It is a stringent work of all.   One should exactly follow the Standard Operation Procedure (SOP) of an instrument.   The awareness of certain safety is, as important as learning how to tolerate with each of other students who are doing the same or another experiment in the same laboratory.

The main idea for the thesis is the adhesion properties of raw rubber-based adhesive as described in the main title above.   The peel strength of rubber-based adhesive is discussed throughout NRs, ENRs and synthetic rubber, EPDM in addition of different resin concentration.   The influence of mastication time on rubber and rubber-based adhesive as well as the effects of varying thickness of adhesive which is applied onto the substrates, are investigated.

Apart from Peel Test, there are two other tests, viz. Tackiness Test and Shear Resistance Test, of which using the same or other instruments depending on the needs. The involved parameters are quite the same as described above but giving significantly different results after having testing for each test.   Comparison of adhesion strength was made for rubber-based adhesives, in accordance with different mastication time, resin concentration and surface thickness of adhesive on sample.

The experimental's objectives are to:

I.   Develop ENRs, SMRs and EPDM-based adhesives, by blending different resin content to raw rubber solution and the effects of resin on the adhesion properties were studied;

II.   Masticate raw rubber using two-roll mill and to coat rubber-based adhesive on the substrate (PET);

III.   Test each rubber-based adhesive sample or specimen by means of different testing modes in accordance with Standard Operation Procedure (SOP) and American Standard for Testing and Materials (ASTM);

IV.   Determine or measure viscosity, tackiness, shear resistance, and peel strength of rubber-based pressure sensitive adhesive (PSA) from a variety formulations; and to

V.   Make comparison between results of testing.

CHAPTER 2 – LITERATURE SURVEY

2.1 Historical Background on Rubber

A rubber tree has a long and rough trunk, with dark-green leaves on the top. Rubber seed, all in three, hiding in a rubber shell when cracks, it drops on the ground, a new life begins.   The latex is found in trunk and in the leaves as well.   Latex (white fluid) shows its nature of tacky.   This milky white fluid is a colloidal suspension of rubber in a liquid consisting mostly of water.   This fluid tends to harden upon air exposure, within a couple hours.   Therefore, the rubber estate worker will go to collect it as fast as possible few moments after tapping in the early morning.

Rubber divides into two, natural rubber (NR) and synthetic rubber.   Standard Malaysian Rubber (SMR) and epoxidized natural rubber (ENR) are belonged to NR whilst EPDM is one type of the latter.   Rubber ball from weeping wood of Haiti origin, was first brought back by Christopher Columbus to Europe (Spain) as early as 1496 ago. Though comprising waterproofing usefulness for cloth and footwear, this gum or rubber ball remained suffering from stickiness in hot weather and brittleness in cold.   Until 1770, the English chemist, Priestley, gave a name 'rubber' to the raw material as it conferred rub off characteristics towards pencil marks.   He may have unawaredly became the first one to add carbon black to rubber (Morton, 1987a; Treloar, 1975).

In the early 1800's, a Scotsman, MacIntosh, had created the first raincoat, by inserting a layer of rubber in between two separate cloths.   Also, the first rubber band had also been invented by cutting rubber into long strips, through Thomas Hancock in 1823.   Until 1839, Hancock and Charles Goodyear from America had not coincidently found that rubber may be improved by addition of sulphur in the presence of heat.   The

new product of so called vulcanized rubber, was not temperature dependant.   Thomas Hancock again made solid tyres for the carriage of Queen Victoria seven years later. Perhaps that was the starting moment for our recent vast tyre industry.

Rubber tree, *Hevea brasiliensis* (Kawahara *et al.*, 2000), was first came to Singapore and Malay Peninsula (now Malaysia Peninsula), in 1877 and 1888 respectively, an effort by Sir Henry Wickham.   After taking over the duty of Sir Henry Wickham, Ridley, H.N. had intended to plant slow-growing rubber trees replacing coffee crops in Malaya.   Hectares and hectares of land and forest had been cultivated for rubber tree crops since then.   He also anticipated that an unprecedented demand on rubber throughout the world will possibly due to the development of newly invented pneumatic tyre (by Thomson, R.W., in 1845), credited to John Dunlop in England.   He was right as increasing market value had made possible for rubber to expand rapidly throughout the world for a great variety of uses until these days.   The demand of rubber increased sharply during the World War I.

Germany had produced methyl rubber during the period of World War I but production of which ceased after recovery of supplies of NR.   Era of synthetic rubber since then, Buna S and Buna N (modern form called as SBR and NBR), polychloroprene (Neoprene), polysulphide rubber (Thiokol), butyl rubber, and silicone rubber lastly had been commercially produced in 1944.   World War II broke out in 1939 and it was not until mid-1941 and early of 1942, United States of America had produced a synthetic rubber of the Buna S type in a slow starting (Craig, 1969).

Rubber is mostly used for tyre making (Kim *et al.*, 2000), parts in automotive, shoe, etc.   Synthetic rubber has gradually developed but not to take over the role of NR, where to some extent, this rubber possesses the suitability for some other special uses. Synthetic rubber could be produced massively, and hence reduces production cost.

Besides, the required properties may also be controlled.   It is, however, NR has higher gel content (Li *et al.*, 2000), higher cohesive strength and tack in the unvulcanized state, high tensile strength and crack growth resistance in vulcanized state (Kawahara *et al.*, 2000), and higher molecular weight (M_w), than synthetic rubber.   All these imply that better adhesion properties, and rubbery behaviour making possible for NR to withstand steadily until today.

2.2 Standard Malaysian Rubber (SMR)

Despite numerous local socio-economic and global recession problems, and the fact that the country's cultivated land has been reduced to 40 % of its original acreage, Malaysia remained the world's largest producer of raw rubber, in the last decade, not only in quantity but also in quality (Buist, 1987).   Malaysian government, through its Rubber Research Institute of Malaysia (RRIM) agency, has produced better and high yields of planting materials or rubber clone by Ong (2000), new tapping and exploitation methods like mechanical tapping knives, polybag collection, new and improved grades such as Standard Malaysian Rubber General Purpose (SMR GP), new and more systematic and efficient mini-estates management, and other advantages (Gullen, 1987).   Recently, the Malaysian Rubber Board (MRB) official physical price for NR in sen per kilo for tyre grade SMR 20 has increased to 690.00 compared to only 459.00 nine months ago, by a pleased rise of sharply 231.00 sen, for rubber estate owner. Details could be referred to *The Star* daily newsprints dated 22nd March, 2006.

In between 1950's and 1960's, the work of Prof. Karl Ziegler and Prof. Giulio Natta in the field of stereospecific polymerization has opened up a vast area in polymer synthesis and there are now available *cis*-, and *trans*-polyisoprene, EPDM, *trans*-polybutadiene and polybutadienes with low and high *cis*-content (Ciesielski, 1999;

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Morton, 1987a). Polyisoprene, a type of diene polymer builds up NR. There are

several thousand units of C_5H_8 in NR.   The single unit, isoprene has 2 carbon-carbon

double bonds.

$$H_2C= \underset{\underset{CH_3}{|}}{C}-HC=CH_2 \longrightarrow \text{ } \mathrm{www}\,CH_2-\underset{\underset{\quad}{\overset{\overset{CH_3}{|}}{\quad}}}{C}=CH-CH_2\,\mathrm{www}$$

Isoprene (C_5H_8)   **Polyisoprene**

$$\left(\begin{array}{c} H_2C \quad\quad CH_2 \\ \diagdown \quad\quad \diagup \\ C = C \\ \diagup \quad\quad \diagdown \\ H_3C \quad\quad H \end{array}\right)_n$$
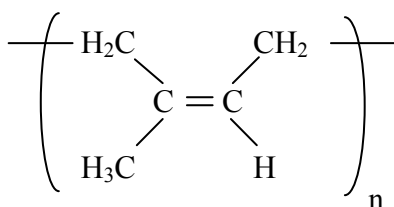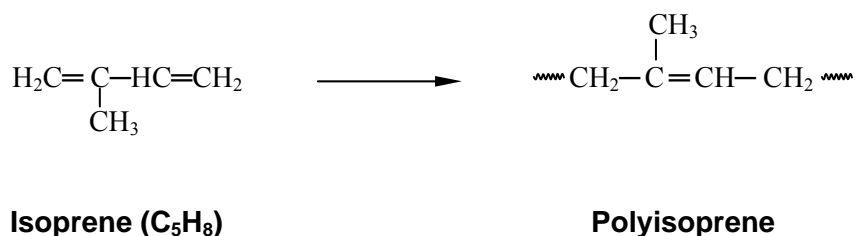
**Scheme 2.1: Ziegler-Natta Reaction (Upper); SMR from *Cis*-1, 4-Polyisoprene
Structure (Lower)**

Rubber from *trans*-1, 4-polyisoprene is not preferably for further enhancing as it is a

tough, horny substance at room temperature (T_r), and will become soft and tacky only

when warmed to about 100°C.   Most of these rubbers obtained from the sap of trees of

the *Sapotaceae* family, which can be found abundantly in Southeast Asia.   The raw

rubber of commerce (sheet, crepe, or block rubber) comprises a M_w mainly in the range

of 500,000 to 1,000,000, with extensions into both lower and higher regions (Allen and

Bloomfield, 1963; Nair and Sekhar, 1967; Ng and Schulz, 1969).

SMR is Malaysian-made, and is named so by 1965. For nearly a half century,

SMR is continuously, observed under the RRIM.   SMR, a type of natural rubber has

been examined for its usability and quality in packing, grading, tape and labelling,

electricity, oil and air resistance, etc.   There are existed in many grades, such as SMR 5, SMR 5L, SMR 10, SMR 20, SMR 50, SMR EQ (light colour; ≤ 0.02 % dirt content), SMR GP, SMR CV, SMR LV, etc., among the most easiest gained in the market, covering a wide range of applications.

The grade of SMR is basically determined by its cleanliness or maximum dirt content and the extent of some other foreign contaminants, such as copper, manganese, nitrogen, and volatile constituents.   They came in very small percentage and seemed nearly the same for each grade of SMR.   Reversely in the case of SMR 10, 20, and SMR 50, they contain even higher percentage of ash and dirt than others, of which 0.1, 0.2, and 0.5 %, respectively.   The bigger the number of SMR, the lower quality and lower rubbery behaviour performed in rubber.

Most of SMRs are produced in a crumb form by one of several mechanical or chemical processes.   After washing and drying either by air or under sunlight or assisted heat, the crumb rubber is compressed hydraulically into 60 – 75 pound (lb) bales (not exceeding 112 lb).   It is then wrapped in polyethylene bag and ready for shipment in big mass.   Advantages of recently new SMR products as recognized by customers outside of Malaysia, are including higher uniformity, greatly improved cleanliness, and better appearance, as well as ease of handling from the producing workplace.

2.3 Epoxidized Natural Rubber (ENR)

Technology of ENR developed since as long ago as 1922, while NR was reacted with a peroxy acid.   But as a result, there was a weakness encountered on structure where it supposed to be.

Until early of mid-1970's, epoxidation was carried out in the latex phase, and the relatively low cost of reagents involved.   Between this, secondary ring-opening reaction involved in the presence of epoxide group.

ENR is a *cis*-1, 4-polyisoprene with epoxide groups randomly allocated along the polymer backbone.   The epoxide group in ENR plays a main role in rubber-based adhesive.   ENR possesses high strength that can be increased by increasing epoxide contents, mostly in between 25 and 50 mole %.   This is because of its ability to undergo strain crystallization, comprising higher glass transition temperatures (T_g) (Poh *et al.*, 2001) and solubility parameter.   Besides, ENR is tested to have increased oil resistance, enhanced adhesive properties, high degree of damping and reduced gas permeation (Gelling *et al.*, 1991).   It means ENR could not be oxidized easily in the presence of air and thus prolongs its shelf life.

ENR is synthesized by epoxidation reaction on the polyisoprene backbone of NR (*Hevea brasiliensis* type) at the latex stage in a suspension containing a significant amount of gel particles, with peracetic acid (Gelling, 1991).   Glacial acetic acid and hydrogen peroxide added in epoxidation process is by Mounir El Sayed *et al.* (2002). Those particles will tend to cause heterogeneity in sealant and adhesive formulation. Thus, ENR has to be degraded chemically using peptizers or physically through mastication.   Degraded ENR could be soluble in most common solvents like toluene and methylenechloride indicating a tacky surface and a transparent appearance. These are depending on mastication time, set temperature, and the model and type of two-roll mill used.

Li *et al.* (1998), in their published paper, mentioned that the ways in producing such an epoxidized natural rubber latex (ENR L) or more precisely ENR.   The raw rubber, NR latex is first added stabilizer and followed by solution of formaldehyde in stirring.

After 10 min, the latex solution is put in hydrogen peroxide and formic acid. A continuous stirring and heating up to $50^{\circ}C$ is necessary. The reaction is kept in attention for another 24 h, to prepare required ENR L. Purification is applied for 24 h afterwards through a dialysis process in deionized water, which should be changed every 2 h in a pH value of 7 at the end of dialysis. ENR L is coated on a clean glass and is put in the vacuum chamber at T_r until a transparency looking latex film is gained. The test sample of ENR L is prepared after removing of water, and is tested to comprise 50 mole % of epoxide group within it.

ENRs that furnished by Guthrie Company, Malaysia, are brought in Universiti Sains Malaysia (USM) together with SMRs, EPDM and some other laboratory grade chemicals. ENR is a new, commercialized polymer in Malaysia since the end of 1987. Such ENR is a potentially useful material, which exhibits unique properties such as good oil resistance, low gas permeability hence giving excellent ageing resistance, increased glass transition temperature, and improved wet grip and friction resistance (Nakason *et al.*, 2004; Hirthammer *et al.*, 1987). At temperature of $20^{\circ}C$, the relative air permeability is ranged from the highest NR, ENR 25, ENR 50, ENR 70, until the lowest synthetic rubber.

70 % of overall rubber (natural and synthetic) consumption is emphasized on the manufacture of the tyres (Kim *et al.*, 2000), belts, cellular products, latex dipped goods, hose and tubing, and footwear, of which assisted by carbon black, rubber chemicals, canvas and textiles, leather and poly(vinyl chloride) (PVC) industries (Sarkar *et al.*, 1990; Parra *et al.*, 2000; Mousa *et al.*, 1998). Technology development will be directed towards new products, but more importantly is new production method that giving good results in higher quality, greater efficiency, and cost effectiveness (Buist, 1987).

Among ENR 10, 25, 50, and 70 mole %, the carbon atom of which is epoxidized by epoxide content, through breaking over the double bond in the backbone of chain system. More epoxide group content means more expensive ENR costs. For the commercial purposes, ENR 70 is seldom use as a sealant or an adhesive compared to those of ENR 25 and ENR 50 (Dynaprene as trade name) (Hirthammer *et al.*, 1987). Some researchers from India, and Japan as well as Europe Countries imported Epoxyprene 25 (ENR 25) and Epoxyprene 50 (ENR 50) from Malaysia.

Apart from SMRs and synthetic rubber, ENRs are also belonged to the group of elastomers or thermoplastic elastomers (TPEs) but not for synthetic ones. TPE here refers to a group of materials, based on a dynamically vulcanized elastomer and a thermoplastic, commonly polypropylene.

TPE based on ENR, has covered a wide range of hardness for related product. Tensile and tear properties are typical of dynamically vulcanized blends of elastomers and polypropylene, while exhibiting excellent oil resistance and air aging properties as mentioned repeatedly above.

TPE has also been produced by blending ENR and a styrene-acrylonitrile (SAN) copolymer. Observing that tensile, tear strength as well as abrasion resistance increased with increasing SAN content. However, there is decrease in elongation at break and lower impact resistance. This is partly owing to the ability of ENR to undergo strain crystallization, and thus suggests a wide range of potential applications through R & D works in rubber industries (Fisher, 1987).

2.3.1 Epoxidation

NR Latex   **ENR**
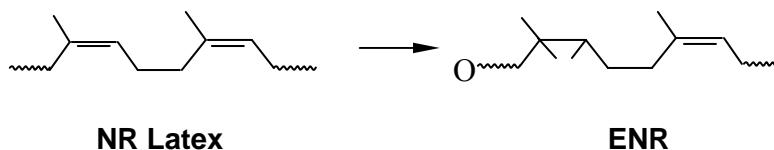
Scheme 2.2: General Schematic of Epoxidation on NR Latex

NR undergoes epoxidation under a random fashion. At a very low level of epoxidation, the reaction becomes easier as isolated isoprene units 'freely' arranged along the main chain of molecule. However, the reaction rate is rapidly increased with increasing peroxy acid content and thus provides more epoxidized blocks up to 15 mole % or above along the backbone of modified ENR.

It is important to know that the epoxidation reaction is a random process and therefore epoxide-activated double bonds are distributed randomly along the polymer molecule. This is proved by NMR spectroscopy studies. ^{13}C-NMR or ^{1}H-NMR studies have also established that in spite of the physical heterogeneity of latex systems epoxidation is quite random. The higher the concentration of the epoxide group in the rubber chain, the stronger is the activation of the adjacent double bond (Poh *et al.*, 1991; Poh *et al.*, 2000).

2.3.1.1 *In Situ* Epoxidation

The epoxidation rate increases with increasing latex concentration. There are various methods involved in epoxidation of NR latex. One of them is through *in situ* generating by using performic acid, an effort of combination of formic acid and hydrogen peroxide. This is a famous method for commercial ENR use. Dilute latex with 20 %

of solid content is preferably to epoxidation of NR but higher solid content up to 60 % for commercial purpose, will result in enhanced reaction rates, and greater output per unit volume of input.

Vernekar *et al.* (1992) reported in their paper that both ^{1}H- and ^{13}C-NMR studies showed that latex concentration has no effect on the sequence distribution of the polymer (epoxide groups).   Even at higher latex concentrations, epoxidation led to reasonably random placement of epoxy group along the chain.

In situ epoxidation has widely adopted for preparation of ENR in two separated reactions.

$$HCOOH + H_2O_2 \rightleftharpoons HCOOOH + H_2O \qquad \textbf{(1)}$$

$$HCOOOH + \text{[NR Latex]} \longrightarrow \text{[ENR]} + HCOOH \qquad \textbf{(2)}$$

NR Latex   **ENR**

$\xrightarrow{+\ H_2O}$

+

Trans-diol
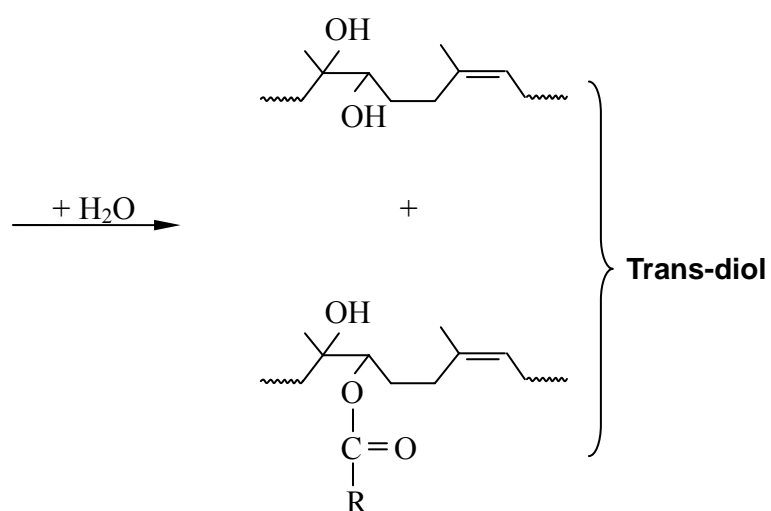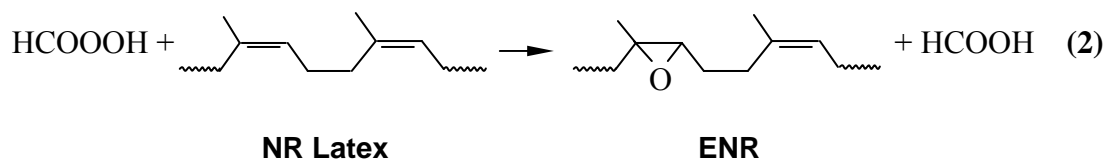
Scheme 2.3: Simple/Low Level of Epoxidation of NR Latex Using Peroxy Acid via Secondary Ring-Opening by Isolated Epoxide Groups

Trans-diol + ENR $\longrightarrow$

$$X = RCOO$$
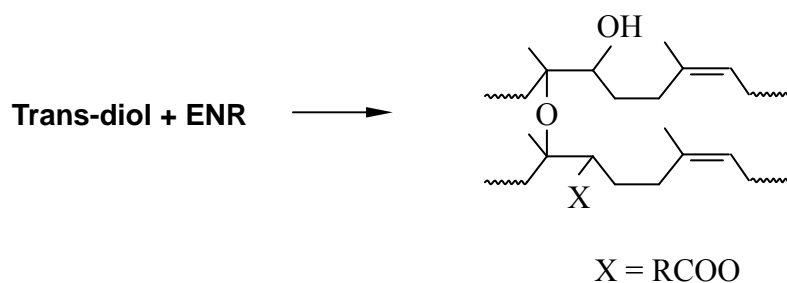
Scheme 2.4: Cross-Linking of ENR via Ring-Opening of Oxirane Groups

15

A systematic change in properties of ENR that observed through the epoxidation whether it is in low or high reaction rate, is depended on the final outcome. In the presence of H_2O, ENR continues to cross-link with ring-opened product yielding interchained ENR through ring-opening of the epoxy groups (Hashim *et al.*, 1995). There are two distinct types of ring-opened products, which basically depended on the level of epoxidation.

As in *in situ* epoxidation, formic acid (HCOOH) is reacted with the hydrogen peroxide (H_2O_2) to form a rate-determining step which also known as a step of the formation of performic acid (HCOOOH – a oxidation agent) as shown in stage (1). The mixture should be stirred continuously until complete conversion of NR isoprene units to ENR. The rate of reaction could be higher with increasing temperature up to $50^{o}C$, heating of which for 10 – 12 h epoxide content of 50 mole % might be attained in ENR. Ratio of H_2O_2 and isoprene units in the backbone determines the degree of epoxidation towards unsaturated sites of yielded ENR. The raw ENRs are macroscopically stickier than both SMRs and EPDM due to their epoxide groups.

HCOOOH in stage (2) tends to react with raw NR towards double bonds along the main chain of molecule. These double bonds are eventually substituted by epoxide groups, on the one hand but not all of them. HCOOH is formed back after completing a 'donation' on the other hand. The reaction rate of peracid (HCOOOH) against double bonds is faster than its formation and the *in situ* epoxidation process will rapidly reach a stationary state which the rate of formation of HCOOOH is equal to its consumption (Bac *et al.*, 1991).

A pure and ideal raw ENR can be obtained by reacting low concentration of HCOOH with a large excess of H_2O_2, without side ring-opening reactions. An ENR product of lower than 50 mole % epoxide content is also a typical elastomer, of opaque

to translucent aspect, with off-white colour bringing visible yellowish outlook. Moreover, ENR of higher epoxide content becomes harder, and less elastic due to increasing gel content. But still ENR is having very good flexibility (lower degree of epoxidation is better). Other than that, it imparts higher abrasion resistance, moderate solvent resistance, low gas permeability, and better peel strength than NR and EPDM.

The polar epoxide group will evidently, tend to change the solubility of ENR. It determines the solving capacity of the initial polyisoprene during the presence of polar solvent. Toluene is a weak but good commercial polar solvent that could dissolve all kinds of raw rubbers in the experiment. The effectiveness of toluene towards SMR and ENR at low degree of epoxidation might not be so vary after all.

2.3.1.2 ENR and Halogen

ENR that derived from NR, has excellent strength, moderately acquired solvent and oil resistance, and gas impermeability properties due to its epoxide contents. Generally ENR, as like NR still poor in aging property. In order to prolong the shelf life of ENR, there is a need to constitute some other elements via halogenation in specialized conditions. The addition of hydrogen has reduced the unsaturation point along the main chain of ENR as in the reaction of hydrogenation that providing hydrogenated epoxidized natural rubber (HENR). The miscibility of blends could be attained via hydrogen bonding.

Apart from this, the reinforcement could be obtained via reaction of secondary ring-opening of epoxide group in ENR resulting brand new products, named halogenated epoxidized natural rubber (XENR). For example in the case of chlorinated epoxidized natural rubber (ClENR – a white solid; transparent looking in

solution) and brominated epoxidized natural rubber (BrENR – a grey powder), they possess a good adhesion properties to metal, glass or ceramics. Chlorine or bromine first attacks the double bonds in ENR and further separation by furanized blocks to propose ring-opening epoxide groups products. These literatures may refer to Roy *et al.* (1993), and Cataldo (1992), in their respective published papers entitled 'Hydrogenation of Epoxidized Natural Rubber' and 'Chlorination and Bromination of Epoxidized Natural Rubber' in details.

HENR tends to reduce the possibility of reactivity of double bonds as it has been saturated by hydrogen (H_2). Furthermore, HENR has signified less gel content created upon aging than that of ENR. The air (oxygen) attacks double bonds in ENR rather than in HENR. And thus as a result, HENR imparts so much better aging properties than that of ENR with low level of epoxidation on the one hand, and comparable to those with high level of epoxidation on the other hand. Moreover, the studies reveal that the higher thermal stability of HENR over ENR, is closely correlated to different content of double bonds existed in respective raw rubber.

Similar to the case of ENR, the original raw NR could also be able to undergo a series of reactions in the presence of bromine or chlorine to give a better adhesion properties form known as brominated natural rubber (BrNR) or chlorinated natural rubber (ClNR), respectively. A detail experimental procedure is also being studied and discussed by Cataldo (1992) in his published paper.

2.4 Ethylene-Propylene Diene Terpolymer (EPDM)

2.4.1 EPDM Background

Ethylene/propylene rubber (usually called as EPDM) had first introduced in the United States, in 1962. Though commercial production only began in 1963, it has grown the fastest among other elastomers. The production had expanded to Europe Countries as well as Japan since then.

Ethylene-propylene diene terpolymer (EPDM) elastomer as classified by ASTM, is a thermoset polymer. EPDM (EPT) is abbreviation for ethylene-propylene terpolymer, in accordance with ASTM D1418-67.

Its backbone is constructed by hydrocarbon chain that consisted of both single and double bonds.

$$
\left(\!\!\begin{array}{c} \overset{\displaystyle CH_3}{|} \\ CH_2 - CH_2 - CH - CH_2 - CH - CH_2 \\ | \\ CH_2 \\ | \\ CH \\ \| \\ CH \\ | \\ CH_3 \end{array}\!\!\right)_{\!n}
$$
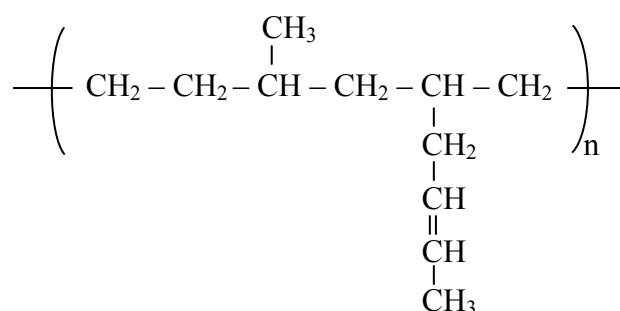
Scheme 2.5: Chemical Structure of Commercially Ethylene/Propylene/1, 4 Hexadiene Terpolymer (EPDM)

2.4.2 EPDM

EPDM has a very low level unsaturation compared to that of NR or ENR, SBR, or NBR, etc.   This polymer is non-tacky, colourless, ranging from 0.86 – 0.87 g/cm^3 of specific gravity.   It is tested to have 0.52 cal/g^{o}C of heat capacity on the one hand, – 95°C of brittle point on the other hand.   Its relative air permeability could be quite similar to that of NR, viz. 100 cm^{2}sec^{-1}atm^{-1}, and obviously higher than SBR (23 % of styrene), 65 cm^{2}sec^{-1}atm^{-1}.   The M_w of an elastomer is commonly reported as the Mooney Viscosity (*ML*).   *ML* of EPDM can vary from a low of 20 to a high 100 (Morton, 1987a).   Furthermore, it is stable during exposure to sunlight, heat, moisture, or ozone, and is possessed extraordinary elongation break up to 400 % without damaging on its original chemical structure (Jablonowski *et al.*, 1991; Kalwara, 1990).

Elongation Break = (Final Length – Original Length) / Original Length x 100 %

EPDM is divided into reinforced and non-reinforced EPDM, two major groups.   The latter is homogenous whilst the former is non-homogenous.   Tensile strength could be carried out in accordance with ASTM D412-68 in the case of homogenous EPDM.

Tensile Strength = Breaking Force / Cross Sectional Area (Ib$_f$/In^2) or (MPa), where
1 MPa = 145 Ib$_f$/In^2 or psi

Non-homogenous EPDM, according to ASTM D751, is measured on breaking of fabric to give a unit of Ib$_f$ or Newton (N) representing the breaking strength since the dimension of length x width has been fixed at one inch.

Moreover, ASTM D624-54 has guided out a specific tear test for non-reinforced EPDM where a specimen is tore by pulling it in the opposite direction at 2 different edges until it tears off.   The result is calculated as Ib$_f$/In or kN/m representing tearing

resistance of specimen.

Similar to the case of breaking strength, by adopting ASTM D751, tearing resistance of reinforced EPDM that could be stood by a sample, is evaluated.   The tearing action is quite the same as in non-reinforced EPDM.   Tearing force is recorded at 5 maximum peaks for the same group of samples and an average is counted.   The unit for tearing strength is written as Ib_f or N.

Both reinforced and non-reinforced EPDM comprise flexibility properties at low temperature, long shelf life, and greater peeling or tearing resistance.   Those are the reasons for EPDM to be utilized widely in roofing, floor layout.   It has been tested and proved that there only less than 1 % of shrinkage of EPDM, by Gish (1990).   Therefore, EPDM is suited for construction and building purposes, especially the roof constructing of which prior to high temperature, continuous heat.   EPDM can easily be rolled over, functioning as insulator on the roof, especially in the West, but very rarely seen in Asia (especially from Southeast).

2.4.3 EPDM in Tyres

EPDM is important in manufacturers of passenger car tyres.   Various components of passenger car tyres, on the selection of compounding recipes has been adjusted to establish tyre fabrication practices due to the tacky problem of EPDM compound.   The formulation of special treatments has also been adopted to overcome the adhesion barrier between cords and carcass stocks to ensure a balance of highway, and city treadwear and skid resistance in conjunction with present-day first grade passenger tyres.   All-EPDM passenger tyre is adequate in durability, safety, and treadwear, as well as the freedom from cracking and checking of the ozone resistant EPDM sidewall

to some extent.

Again, reinforced EPDM by fabric, resin or cement in the presence of toluene, will tend to increase the breaking strength. The fabric could be cotton, rayon, nylon, or from the synthetic ones. In some other formulations, there strictly control over catalyst and accelerator in order to avoid degradation on whole system. A more detail procedure had been demonstrated by Crowther and Melley (1974), in accordance with formulation between EPDM elastomer and polyester fibres.

2.4.4 Tackifier in EPDM

As the nature behaviour of non-tackiness and chemically stable, EPDM faces difficulty to provide appropriate tackiness to most adherents. Resin tackifier or resin that formulated with EPDM is one of many purposes where an EPDM-based pressure sensitive adhesive (PSA) could be produced to suit for certain field of industries.

Generally, resin is added as a tackifier to raw rubber for enhancing tackiness or tackiness characteristics that may not be performed by single raw rubber. Degradation may occur to EPDM and other rubber-based PSA via oxidation, UV rays, and atomic rays on polymer surface.


PSA ⟶

Polymer ⟶

Figure 2.1: A Tape or Label Consisting Raw Rubber-Based PSA and Elastomer

There are various types of resins that could be compatible with EPDM elastomer. Among them are rosin ester, phenolic resin, polybutene, terpene combinations, and combinations between these resins and other hydrocarbons. These resins could be differentiated from their naturally colour, physical appearance, miscibility and curing rate when blending with EPDM.

2.5 Coumarone-Indene (CI) Resin

Coumarone-indene (CI) resin, supplied by Euro Chemo-Pharma Sdn. Bhd., Malaysia, is a mixed compounding thermoplastic polymerized resin between coumarone and indene structure. Coumarone resin is one of natural or wood resins. Coumarone (benzofuran) combines with indene in coal tar naphtha (b.p. $150 - 200^{o}C$) in the presence of other compounds, mainly xylene and cumenes. Resinification is carried out to separate the resin from those compounds followed by distillation to yield a solvent-based CI resin. However, hard and brittle CI resin solid is polymerized by mixing concentrated sulphuric acid or a Friedel-Crafts catalyst to the naphtha at $0^{o}C$. Any found sludge is removed after $5 - 10$ min, and neutralization is followed by then. Residual naphtha is finally washed and distilled off to leave the resin.
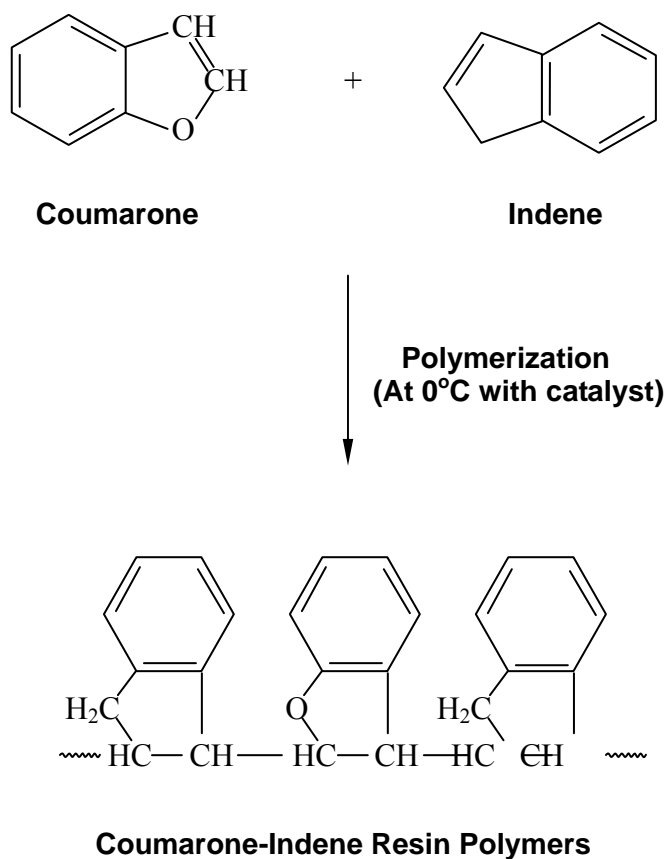
Scheme 2.6: Polymerized Coumarone-Indene Resin Combination Between Coumarone and Indene Structure

The hard and brittle to soft and sticky of resin greatly depends on the relative proportion of coumarone and indene content and polymerization conditions. Usually, the coumarone content is less than 10 %. This resin is a low surface energy polymer due to the bulky part of resin which is extended by peripheral hydrocarbon substituents. It is highly soluble in many organic solvents, including toluene and compatible with a wide range of other polymers.

The resin that characterized by the m.p. below 50°C, could act as tackifier or plasticizer in the mixture with rubber. Tackifier here acts as softening tools whereas plasticizer assists in pigment dispersion apart from holding stress-strain properties at