DEVELOPMENT IN CROSSLINKING SYSTEM FOR NATURAL RUBBER AND EPOXIDIZED NATURAL RUBBER

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งานวิจัยนี้แบ่งออกเป็น 2 สองส่วน โดยส่วนแรกเป็นการศึกษาความเป็นไปได้ในการใช้มาเลอิกแอนไฮไดรด์เป็นสารเชื่อมขวางสำหรับยางธรรมชาติอิพ็อกซิไดส์ อีกส่วนเป็นการศึกษาความเป็นไปได้ในการเตรียมการเชื่อมขวางยางธรรมชาติที่สามารถผันกลับได้ด้วยความร้อนโดยใช้กลีเซลรอล/หรือไดแอททิลีนไกลคอลเป็นสารเชื่อมขวาง ผลการทดลองในส่วนแรกพบว่า ยางธรรมชาติอิพ็อกซิไดส์ ทั้ง ENR25 และ ENR50 สามารถเกิดการเชื่อมขวางด้วยมาเลอิกแอนไฮไดรด์ได้ จากผลการพิสูจน์เอกลักษณ์ของการเชื่อมขวางพบพีคที่ปรากฏขึ้นใหม่ที่เลขคลื่น 1735 cm^{-1} และ 1710 cm^{-1} ในสเปคตรัมการดูดกลืนแสงอินฟราเรด ซึ่งแสดงให้เห็นว่าการเชื่อมขวางระหว่างสายโซ่ของยางเกิดผ่านพันธะเอสเตอร์ ดังนั้นจึงกล่าวได้ว่าการเชื่อมขวางที่เกิดขึ้นเกิดจากปฏิกิริยาการเปิดวงแหวนของหมู่อิพอกไซด์ของยางด้วยหมู่ไฮดรอกซิลของไดแอซิดที่มาจากการไฮโดรไลซิสของมาเลอิกแอนไฮไดรด์ เมื่อทดสอบการบวมตัวในตัวทำละลายพบว่า การบวมตัวจะลดลงเมื่อเพิ่มปริมาณมาเลอิกแอนไฮไดรด์ ซึ่งหมายความว่าระดับการเชื่อมขวางเพิ่มขึ้นตามปริมาณของมาเลอิกแอนไฮไดรด์ นอกจากนี้ยางธรรมชาติอิพ็อกซิไดส์ที่ผ่านการเชื่อมขวางด้วยมาเลอิกแอนไฮไดรด์ยังมีค่าการสลายตัวทางความร้อนและสมบัติเชิงกลที่ดีกว่ายางธรรมชาติอิพ็อกซิไดส์ที่ไม่ผ่านการเชื่อมขวาง จากรีโอกราฟพบว่าลักษณะการคงรูปของยางธรรมชาติอิพ็อกซิไดส์ด้วยมาเลอิกแอนไฮไดรด์เป็นแบบมาร์ชชิ่งและมีอัตราการเกิดการคงรูปในช่วงต้นที่สูงมาก ซึ่งเป็นสาเหตุให้ ENR50 ไม่สามารถขึ้นเป็นแผ่นฟิล์มได้ทัน สำหรับในส่วนที่ 2 จากผลการทดลองพบว่า สามารถเตรียมยางธรรมชาติที่มีการเชื่อมขวางแบบผันกลับได้ด้วยความร้อนจากการใช้กลีเซลรอล/หรือไดแอททิลีนไกลคอล โดยขั้นตอนแรกยางธรรมชาติจะถูกดัดแปรโครงสร้างโดยการกราฟต์มาเลอิกแอนไฮไดรด์ลงไปบนสายโซ่ได้เป็นยางธรรมชาติมาลิแอตด้วยกระบวนการผสมแบบรีแอคทีฟโดยปราศจากการเติมสารริเริ่ม โดยปฏิกิริยาจะเกิดขึ้นจากแรงเฉือน ระดับการกราฟต์สูงสุดที่ได้อยู่ที่ 1.76 % การเกิดของยางธรรมชาติมาลิแอตสามารถยืนยันได้จากการปรากฏของพีคที่เลขคลื่น 1835 cm^{-1} และ 1790 cm^{-1} ในสเปคตรัมการดูดกลืนแสงอินฟราเรด โดยพีคดังกล่าวเป็นของ C=O ที่ปรากฏในวงแหวนซัคซินิคแอนไฮไดรด์ เมื่อทำการทดสอบการบวมตัวของยางธรรมชาติมาลิแอตที่ผสมกับกลีเซอรอล/หรือไดเอทิลีนไกลคอล และให้ความร้อนแล้ว พบว่า การบวมตัวในตัวทำละลายลดลงในขณะที่ค่ามอดูลัสและความทนต่อแรงดึงมีค่าเพิ่มสูงขึ้น แสดงว่าเกิดการเชื่อมขวางขึ้น โดยยางธรรมชาติมาลิแอตที่คงรูปด้วยไดแอทิลีนไกลคอลให้ระดับการคงรูปที่สูงกว่ายางธรรมชาติมาลิแอตที่คงรูปด้วยกลีเซลรอล ผลการพิสูจน์เอกลักษณ์ของการเชื่อมขวางพบว่า เมื่อเชื่อมขวางยางธรรมชาติมาลิแอตด้วยสารเชื่อมขวางทั้งสองชนิดทำให้เกิดพันธะเอสเตอร์ระหว่างสายโซ่ของยางธรรมชาติมาลิแอต ซึ่งเกิดจากการทำปฏิกิริยาระหว่างวงแหวนซัคซินิคในแอนไฮไดรด์และหมู่ไฮดรอกซิลของกลีเซลรอล/หรือไดแอทิลีนไกลคอล เมื่อนำยางที่ผ่านการเชื่อมขวางไปตัดเป็นชิ้นเล็ก ๆ แล้วนำมาขึ้นรูปใหม่ที่ 150 °C พบว่าสามารถขึ้นรูปได้ใหม่มากกว่า 3 ครั้ง โดยค่าความแข็งแรงเชิงกลจะลดลงตามรอบของการขึ้นรูปใหม่

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ลายมือชื่อนิสิต ....
ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

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Nuttida Srirachya : DEVELOPMENT IN CROSSLINKING SYSTEM FOR NATURAL RUBBER AND EPOXIDIZED NATURAL RUBBER. Advisor: Asst. Prof. KANOKTIP BOONKERD, Ph.D. Co-advisor: Prof. TAKAOMI KOBAYASHI, Ph.D.

This research was divided into two parts. The first part was to investigate the possibility to use maleic anhydride (MA) as a crosslinking agent for epoxidized natural rubber (ENR). The second one was to investigate the possibility to prepare the thermoreversible crosslinking of natural rubber (NR) when using glycerol (Gly) or diethylene glycol (DGly) as a thermoreversible crosslinking agent. For the first part, it was found that both ENR25 and ENR50 can be crosslinked with MA. From FT-IR spectra, the emerge of two peaks at 1735 cm^{-1} and 1710 cm^{-1} indicated that the crosslinking was taken place by the ring opening of oxirane ring of ENR with the hydroxyl groups of diacids derived from the hydrolysis of MA. Therefore, the linkages between ENR chains were the ester linkages. After swelling testing, it was found that the value of swelling index decreases with the increase of MA loading. In addition, the crosslinked ENR with MA showed better thermal resistance and higher mechanical properties than the uncrosslinked ENR. Rheographs showed that the cure characteristics of the ENR crossslinked with MA was marching behavior with a very high induction crosslinking rate. This led ENR50 to scorch during molding. For the second part, the results showed that it was possible to prepare the thermoreversible crosslinking of NR when using Gly or DGly as crosslinking agents. To achieve this, firstly NR was grafted with MA using a reactive processing method in an internal mixer without adding an initiator. This gave a product called maleated NR or MNR. The grafting was occurred by the shear action and the highest % grafting was 1.76%. The formation of MNR was confirmed by the occurrence of two peaks in FT-IR spectra at 1835 cm^{-1} and 1790 cm^{-1} attributed to the C=O of the succinic anhydride ring. The results showed after heating the MNR mixed with Gly or DGly, the obtained products had lower swelling index and higher modulus and tensile strength. This was indicated that the thermoreversible crosslinkings of MNR with Gly or DGly were taken place. The FT-IR spectra of the MNR mixed with Gly and with DGly showed that upon heating covalent ester crosslinks were formed. It was proposed here that the thermoreversible crosslinking was formed via a reaction of succinic anhydride ring with hydroxyl groups of Gly or DGly. It was found after remolding the small pieces of rubber at 150 °C the rubber sheet can be newly formed. This indicated that the thermoreversible crosslinking MNR with Gly or DGly can be reprocessed. After remolding, the mechanical properties decreased with increasing recycling round.

Field of Study:	Materials Science	Student's Signature ....
Academic Year:	2018	Advisor's Signature ....
		Co-advisor's Signature ....

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CHAPTER 1

INTRODUCTION

Rubber is a polymeric material with a unique property. It can be elongated several times and returns back to the original shape once removing external force. Amongst all rubbers, natural rubber (NR) has been used throughout the world. This is not only because NR is a green material but also because NR can undergo strain-induced crystallization, thus giving NR in having high green strength and excellent mechanical strength under severe deformations[1]. Due to its high flexibility, abrasion resistance, resilience and tack properties, NR can be used for many applications for example tires, condoms and O-rings[1-3]. However, due to its nonpolar nature and the presence of double bond, NR has a very low resistance to oil and is easily attacked by ozone and oxygen. Thus, a lot of researchers study chemical modification at double bonds by introducing hydrophilic groups along NR backbone to improve the stability of NR and to provide widespread applications. Epoxidation and maleation reaction of NR earns much attention due to the simplicity and effectiveness. The epoxidized natural rubber (ENR) and maleated natural rubber (MNR) have good mechanical properties, excellent chemical resistance, corrosion resistance and good dimensional stability.

Although the chemical modification can enhance the polar nature of NR, NR and all pristine rubbers are sticky, can easily be deformed when warm, and are brittle when cold. In this state rubber cannot be used to make articles with a good level of elasticity. To overcome the problems, discrete rubber chains are chemically linked together to form a three-dimensional network structure with improved mechanical properties and solvent resistance. The mobility of rubber chains in the network is markedly restricted. Therefore, the rubber chains cannot move pass each other easily. This results the crosslinked rubber in having lower elongation but higher resistance to deform. This process is known as vulcanization or crosslinking of rubber[4-7]. The vulcanized rubber is more durable and less sensitive to temperature in comparison to the pristine rubber. Several research articles have been reported previously regarding the industrial application of different crosslinking agents like sulfur[5, 6], organic peroxides[8, 9], radiation[10, 11] and di-functional agents[12-15] in the vulcanization of rubber. Sulfur is widely used to crosslink NR and its modified one. However, sulfur alone is inefficient to form the crosslink. To obtain efficient crosslinking system, accelerator and activator are needed. Thus, sulfur crosslinking system consists of many curing agents. For ENR, due to the presence of active epoxide on ENR, recently many researches pay attention to the use of di-functional molecules such as dicarboxylic acid as a novel crosslinker for ENR[13-16]. However, the properties of the di-functional molecule crosslinked ENR and crosslinking kinetic are still undesirable. Moreover, all commercially available crosslinking agents form the permanent network, thus giving non-recycled or non-reused rubber.

Thus, from an environmental point of view, the crosslinking process is needed to develop. In the recent years, some beneficial studies have been reported in literature to develop thermoreversible crosslinking of rubber using different approaches[17-24]. According to our best knowledge, the detailed study based on the thermoreversible covalent crosslinking of NR is very rare. The development of thermoreversible crosslinking of NR will extend the usage of NR.

Therefore, in this study we are interested in developing a novel crosslinking system for ENR and NR. Two main objectives are focused here. The first objective is to investigate the possibility to use maleic anhydride as a novel di-functional molecule for crosslinking ENR. The second objective is to study prepare thermoreversibly crosslinking NR. The glycerol and diethylene glycol are used as the crosslinking agents.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Rubber (NR)

Natural rubber (NR) is an agricultural product. It is an elastomeric hydrocarbon polymer, which occurs as a white liquid known as latex in the sap of several assortments of plant[25]. The history of NR occurred when Christopher Columbus discover it, during his second voyage in 1493-1496. He found the locals in Haiti playing with balls made from the outflow of a tree called cau-uchu or weeping wood. The term rubber was called by John Priestly in 1770, when he found that the material could delete pencil marks[26]. There are many plants containing latex include Para rubber, Gutta-Percha, Panama rubber, spurges, lettuce, common dandelion, Russian dandelion, Scorzonera tau-saghyz, and Guayule[26]. The commercial source of NR latex is *para* rubber tree (*Hevea brasiliensis*). Production predominately occurs in plantations and manors in south-east Asia, a locale which produces almost 90% of worldwide NR[27]. The latex found in the internal bark of *H. brasiliensis* is gotten by shaving the bark with a sharp cut and collection of latex in cups (Figure 2.1).

Figure 2.1 *Para* rubber tree (*Hevea brasiliensis*)

Latex is a milky fluid of polymer microparticles in a water medium. The content of *Hevea* latex is proteins, alkaloids, starches, sugars, oils, tannins, resins and gums that coagulate on exposure to air[27, 28]. This milky emulsion is collected and then coagulated to yield high molecular weight (Mn > 1 million g/mol) polymer. The productivity of *Hevea* trees is around 50–100 g latex per day in a full-grown tree. Depending on the seasonal effects and the state of the soil. NR derived from *Hevea brasiliensis* is predominantly establish of cis-1,4-polyisoprene $(C_5H_8)_n$ (Figure 2.2) where "n" may range from 150 to 2,000,000[28]. The obtained latex is commercially transformed to both centrifuged latex and rubber sheets. The adding of formic acid can solidify latex rubber. After that pressed it between the two-roll mill to remove excess water and form a sheet[28]. The properties of NR show in Table 2.1.

Table 2.1 The properties of NR

Item	Attribute	Properties
Physical properties	Glass transition temperature (°C)	-70 °C
	Melting temperature (°C)	25 °C
	Hardness range (Shore A)	30 – 100
	Maximum elongation (at 70 °F)	750
	Specific gravity	0.915
	Solubility	Insoluble in water, alcohol, acetone, dilute acids and alkalis; soluble in ether, carbon disulphide, carbon tetrachloride, petrol and turpentine
Tensility	Tensile strength before break	Very strong 2475 psi
	Maximum tensile strength (at 70 °F, psi)	13.9 N/mm^2
Vulcanization	-	At 307 °F / 152 °C
Advantages	Physical resistance	Excellent resilience Excellent tear strength Excellent abrasion resistance Excellent impact strength Excellent cut growth resistance
Advantages	Environmental resistance	Excellent water resistance Good low temperature flexibility Good oxidation resistance
	Chemical resistance	Good resistance to alcohols and oxygenated solvents Good resistance to acids
Limits	Environmental resistance	Poor ozone resistance Poor sunlight resistance Very little flame retardance
	Chemical resistance	Poor oil and gasoline resistance Poor resistance to (aliphatic and aromatic) hydrocarbon solvents

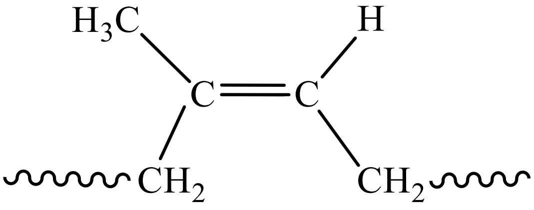


Figure 2.2 Structure of cis-1,4-polyisoprene

2.2 Chemical Modification of NR

Commercial NR or cis-1,4-polyisoprene is currently the only natural rubber resource. It is an important material in the rubber industry, particularly for the manufacture of rubber tires. NR possesses excellent physical properties including high elasticity, high tensile strength and low heat build-up. But NR also has some undesirable properties such as low heat and abrasion resistance and poor ageing properties, as well as low oil and flame resistance[27]. These drawbacks may be due to the high unsaturation of the molecular chain, the non-polar character of natural rubber and the presence of allylic carbons[29]. To overcome these disadvantages, the NR is treated by chemical modifications. During chemical modifications, changes in molecular structure are taken place. Some samples of chemical modifications are hydrogenation and grafting.

The fundamental reason of chemical modification would be to present useful pendent groups to supply new methods of crosslinking or grafting on polymeric side chain. Improved bonding to glass, metals and textiles, modified abrasion and enhanced resistance to aging. The updating of physical properties for example oil resistance and air permeability could empower NR as a renewable resource to replace some oil-based specialty synthetic rubbers[30].

Chemical modifications on NR are often produced in either solid, solution or latex state. The modifications are classified into 3 categories:[29]

- Modification by bond arranging without introducing new groups. This kind of modification can result in changes within the structure and/or reduction in molecular weight of NR. Cyclization is an example of bond arranging.
- Modification by introducing atom or chemical group like chloride, hydrogen, nitrogen and epoxy via addition or substitution reactions at the olefinic double bonds. The outcome of modified NR can possess the properties of the new chemical groups. For instance, epoxidized NR shows higher hydrophilicity and glass transition temperature.
- Modification by grafting with molecules, typically vinyl monomers at the allylic carbon. The grafted polymer will either have low or high molecular weight. One of the most potential grafting reagents easily taken place onto NR is maleic anhydride (MA).

2.2.1 Epoxidized natural rubber (ENR)

Epoxidation of NR is carried out by converting the carbon-carbon double bond into oxirane rings[29]. Epoxidation of NR latex usually used peracid where the peracid can either be prepared separately or formed in situ from a precursor using acid and hydrogen peroxide. Figures 2.3 (a) and (b) show the epoxidation of NR with peracid prepared separately and in situ, respectively[27].

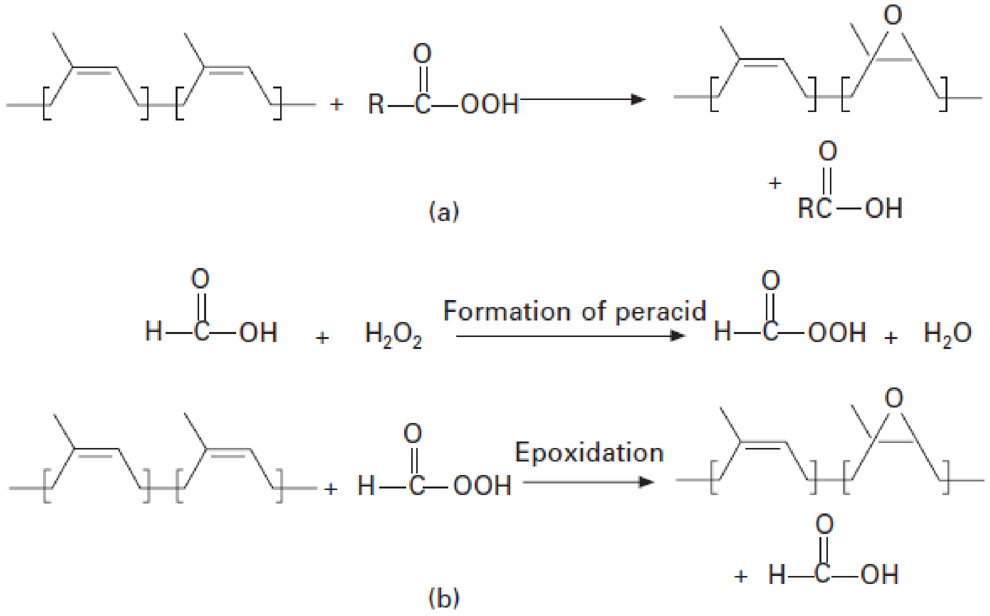


Figure 2.3 *(a)* Epoxidation of NR with peracid and *(b)* in-situ performic acid generated from the reaction of formic acid and hydrogen peroxide

Commercial production of epoxidized NR (ENR) has been carried out in Malaysia since 1988, for example, ENR10 (having 10% mole of epoxide content), ENR25 (having 25% mole of epoxide content) and ENR50 (having 50% mole of epoxide content). However, the properties of ENR10 closely resemble those of NR and it was later withdrawn from the market[27]. Two grades are available under the tradenames Epoxyprene 25 and Epoxyprene 50. Depending on the degree of epoxidation, ENR may have a wide range of properties. Higher modification levels increased the hardness of the rubber. It was found that with less than 50% epoxidation, the products are elastic and have an off-white color. An increase of epoxide content also increases the gel content[27]. For every 1 mol% epoxidation, the glass transition temperature (Tg) increases by approximately 1°C, thus ENR25 has a Tg of -47 °C and ENR50 has a Tg of -22 °C[31]. ENR has a higher Tg compared to NR, thus giving higher damping, better air permeability, higher hysteresis, better wet grip as well as higher polarity[29]. The solubility of ENR depends on the level of epoxidation and the nature of the solvent[31]. ENR not solely maintains the elasticity of the initial NR even at modification more than 20% mole but also opens the opportunities to utilize the oxirane groups in numerous chemical reactions. These reactions enclosed novel crosslinking systems and reinforcement systems.

The epoxy groups of ENR are reactive towards nucleophilic reagents, including acid, base and alcohol. ENR can therefore be converted to other functionalities by the epoxide ring opening reaction. The incorporation of aromatic amine antioxidants into the molecular chain of ENR may be done through the oxirane group. ENR modified in this way shows an improvement in oxidation resistance. The hydrolysis of ENR under acidic or alkaline conditions results in a partial conversion of the epoxide ring into a diol derivative. The resultant product may be further degraded using lead tetra-acetate to produce functionalized low molecular weight rubber[27]. ENR can be vulcanized with typical sulfur vulcanizing systems, peroxide, amine compounds, aminosilanes, radiation and moisture[27, 29, 31].

2.2.2 Maleated Natural Rubber (MNR)

The grafting of maleic anhydride (MA) onto the molecular chain of NR is known as maleinization or maleation. The reaction of MA with NR may occur by two ways: through radical reaction and double bond reaction (ene reaction). The grafting of MA into NR by radical reaction was reported in 1939 by Bacon and Farmer who used benzoyl peroxide as a radical initiator[27]. It was anticipated that MA would react over the double bond of NR, utilizing two adjacent or non-adjacent double bonds. In this case, the reaction of MA with the rubber happened at the allylic carbon as there was no loss of unsaturation in the NR chain. The proposed structure was the connection of the MA as a pendant group on the rubber chain.

A mechanism of radical reaction was shown in Figure 2.4[32]. This can be identified by two characteristic signals of C=O of a cyclic five-membered ring of anhydride at 1835 cm^{-1} (asymmetric stretching) and 1790 cm^{-1} (symmetric stretching). However, an absorption signal around 1710 cm^{-1}, which can be attributed to a carbonyl group of carboxylic acid, was also observed. This may be due to the anhydride ring opening reaction caused by the reaction with nonrubber constituents in NR such as fatty acids and proteins[33].

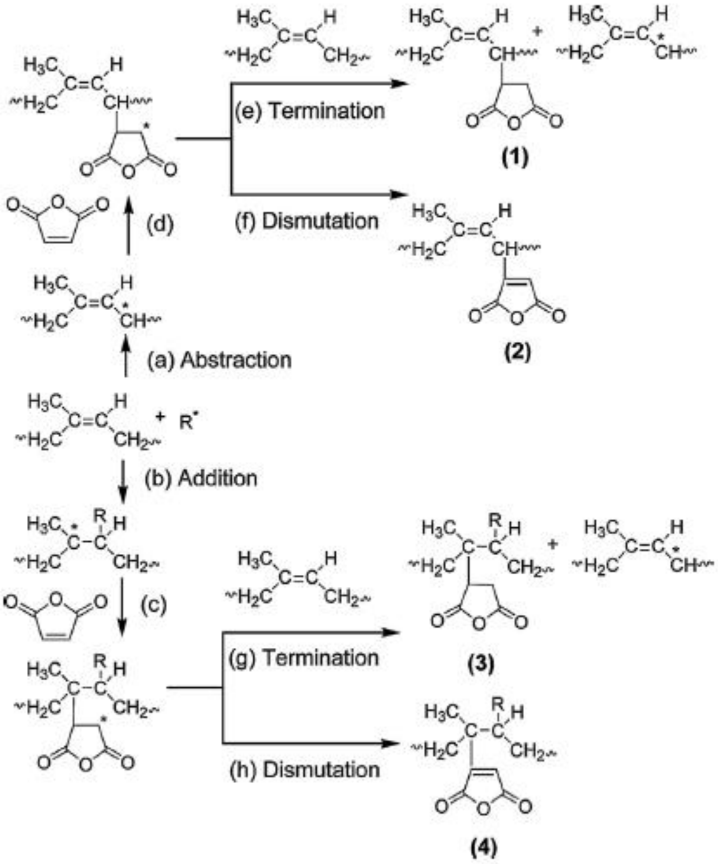


Figure 2.4 Reaction of NR with MA via radical reaction

In the ene reaction, the double bond of MA is considered as an electron-deficient alkene which is prone to react with an electron-rich alkene such as NR. The reaction mechanism is processed via pseudo 4+2 cyclo-addition. The C=C of MA acts as an unsaturated enophile (X=Y) which reacts with the allylic proton of NR, forming an electrocyclic reaction[27]. The resultant product is an allylic substitution of X=Y with movement of the double bond. The double bond of the resultant product can be out-of-chain or in-chain, depending on the steric factors. The reaction of MA with NR via the ene reaction can be obtained at high temperatures (180–230 °C) in the absence of catalyst or initiator.

It was later shown that other catalysts like azodiisobutyronitrile (AIBN), and peroxides can be used to react MA with polyisoprene rubber[27]. Investigation of the grafting part of MA into a polyisoprene block styrene isoprene block copolymer was carried out by a solution system within the presence of AIBN at around 70 °C[27]. This affirmed that the MA grafting had continued through substitution at the allylic position. Vulcanized maleated rubbers have prevalent solvent resistance, flex cracking resistance and ageing resistance than conventional natural rubber vulcanization. Nonetheless, these properties are comparable with those of synthetic polymers for example ethylene-vinyl acetate copolymers, polyurethane and plasticized PVC. No industrial development of maleated NR vulcanizates has been reported[27].

2.3 Vulcanization of NR

The vulcanization method is essential to create most valuable rubber articles, like tires and mechanical products. Un-vulcanized rubber is usually not strong and does not retract basically to its original form when extremely deforming, and it is often exceptionally sticky. In brief, un-vulcanized rubber will have an equivalent consistency as chewing gum[5, 6]. Vulcanization could be a crosslinking reaction by sulfur or alternative vulcanizing agents that makes three-dimensional network structures in rubber and is that the known method of giving rubber products greater stability. Vulcanization was found by Charles Goodyear in 1839 a while recently the development of the conception of macromolecules of Hermann Staudinger in the 1920s[34].

Vulcanization could be a method usually applied to rubbery or elastomeric materials in order to enhance the retractile force. Therefore, the vulcanized rubber can return closely to their original shape once a massive mechanically imposed deformation is removed. Vulcanization will also be defined as a method that will reduce the number of permanent deformations remaining when removal of the deforming force. Thus, vulcanization increases elasticity whereas it decreases plasticity. Chemically, it is usually accomplished by the formation of a vulcanized network[5, 6].

Vulcanization causes extremely significant changes at the molecular level. The long rubber molecules become joined alongside crosslinks spaced on the polymeric chains, with the typical distance between junctures corresponding to a molecular weight between crosslinks. Since of network formation, the rubber becomes basically insoluble in any solvent, and it cannot be processed by any technique that requires it to flow. In this way, it is fundamental that vulcanization must happen only after the rubber article is in its final geometric shape. Effects of vulcanization on end-use properties[6] are shown in Figure 2.5. It ought to be noted that static modulus increments with vulcanization than does the dynamic modulus. The dynamic modulus could be a composite of elastic and viscous behavior, while static modulus is essentially a measure of solely the elastic component of rheological behavior. Crosslink formation significantly decreases hysteresis. Hysteresis is that the proportion of the rate subordinate or viscous component to the elastic component of deformation resistance. It is moreover a measure of deformation energy, which is not stored but is changed over to heat. Therefore, vulcanization causes a trade-off of elasticity for viscous or plastic behavior. Tear strength, fatigue life, and toughness are associated with the breaking energy. Value of softness properties increase with little amounts of crosslinking however they are reduced by further adding crosslink. Properties associated to the energy to break increase with increases in each the amount of network chains and hysteresis. Since hysteresis diminishes as additional network chains are created, the energy-to-break related properties are maximized at few intermediate crosslink density. It ought to be noted that the properties given in Figure 2.5 are not capacities as it is of crosslink density. The type of crosslink and polymer and also type and amount of filler also play important role on them. Reversion could be a term typically applied to the loss of network structures by nonoxidative thermal aging. It is ordinarily related with isoprene rubbers vulcanized by sulfur. It is the results of too long of a vulcanization time or of hot aging of thick areas It is most extreme at temperatures over around 155. °C It happens in vulcanizates containing large number of polysulfidic crosslinks. In spite of the fact that its mechanism is complicated, the chemical changes that happen throughout the reversion of natural rubber has been found. In some cases, the term reversion is connected to different types of nonoxidative degradation, particularly with regard to rubbers not based on isoprene[5, 6].

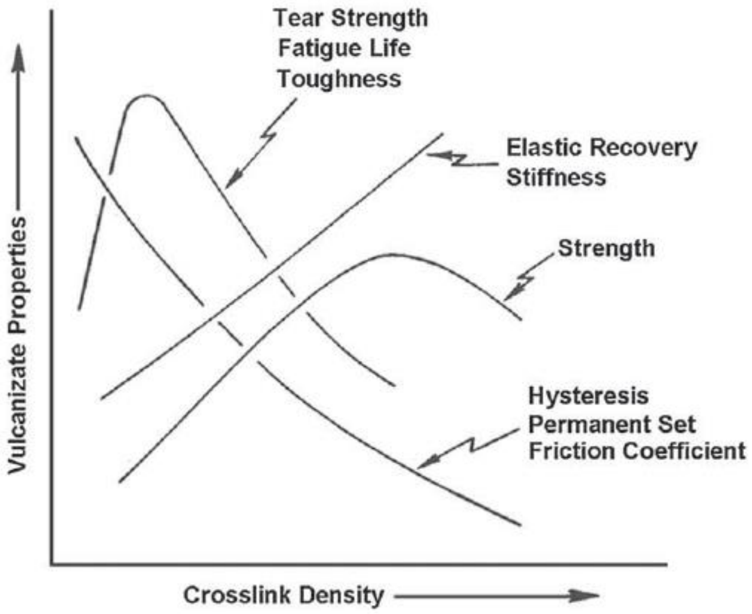


Figure 2.5 Vulcanizate properties as a function of the extent of vulcanization

2.3.1 Sulfur Vulcanization

Sulfur vulcanization could be a crosslinking reaction by sulfur that produces three-dimensional network structures[34] (Figure 2.6) in rubber and is that the known prepare of giving rubber products more noteworthy stability. Sulfur crosslinking reactions are progressed by successive advancement in accelerators, activators, retarders, and others, to enhance processability and mechanical properties[34, 35].

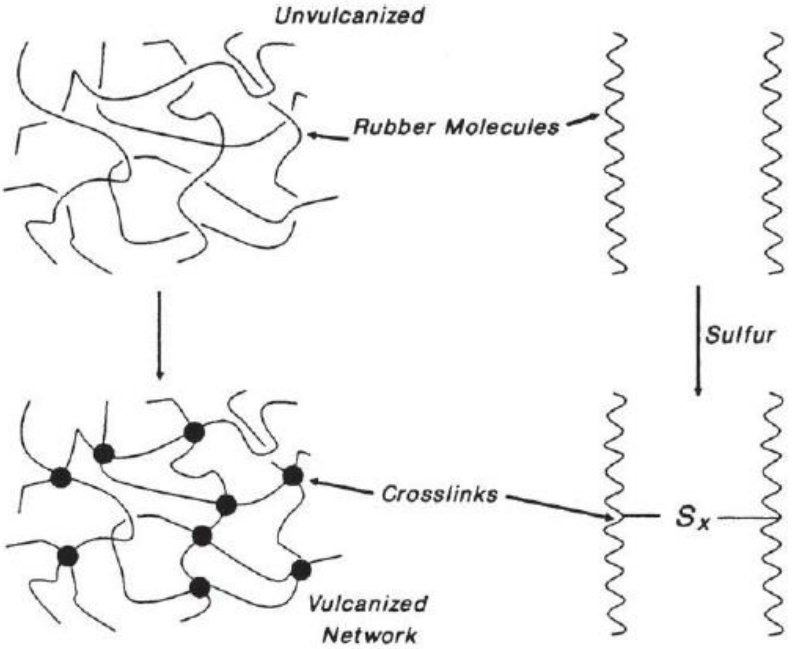


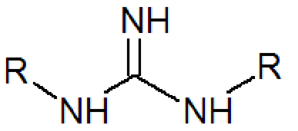
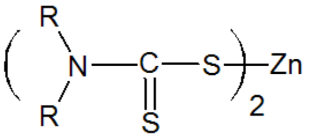
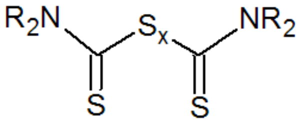
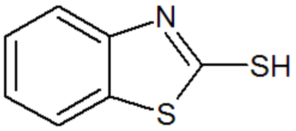
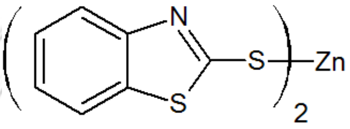
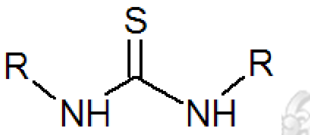
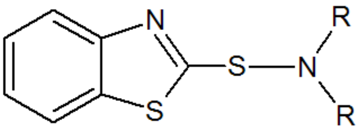
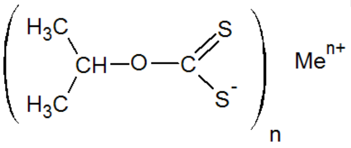
Figure 2.6 Network formation of sulfur vulcanization

2.3.1.1 Accelerators for Sulfur Vulcanization

Vulcanization of rubber by only sulfur is greatly slow and may take many hours at 140 °C or higher. This is complicated since long exposure to temperature and oxygen leads to oxidative degradation, leading to the destruction in mechanical properties. To reduce rubber degradation and to accelerate the vulcanization process, accelerators are ordinarily employed. An accelerator is characterized as a compound that increases the speed of vulcanization which allows vulcanization to proceed at lower temperature and with larger productivity. Accelerator furthermore decreases the quantity of sulfur required to crosslink the rubber, enhancing the aging properties of the vulcanized rubber. A few of the accelerators also function as sulfur donors and therefore permit vulcanization to continue at lower sulfur substance[36, 37].

A wide range of chemicals that have a place to various chemical categories are familiar to accelerate rubber vulcanization, in any case, only around 50 accelerators are utilized on a commercial scale. Most of those are appeared in Table 2.2[4]. The accelerators will be additionally classified as primary and secondary accelerators. The primary accelerators are ordinarily utilized at 0.5 to 1.5 phr. The vulcanization speed of this group will run from slow to ultrafast counting on composition and sort of accelerator. Ordinary primary accelerators embrace thiazoles and sulfenamides whereas thioureas and dicarbamates will operate as each primary and secondary accelerator. Some other curatives like sulfenamides are quick cure and cause a delay within the onset of vulcanization that is commonly desired in rubber process as a result of it will increases the scorch time. The accelerators such as guanidines, thiurams and dithiocarbamates are used as secondary accelerators to activate the primary accelerators. The secondary accelerators use for increases the speed of vulcanization.

Table 2.2 The accelerators for sulfur vulcanization

Compound	Chemical Structure	Side Groups (R)
Guanidine (Moderate)		R = Phenyl, Toluoyl R = Alkyl
Dithiocarbamate (Very fast)		R = Phenyl, Toluoyl R = Alkyl
Thiuram (Very fast)		R = Alkyl
2-Mercaptobenzothiazole (Moderate)		
Zinc-2- Mercaptobenzothiazole (Very fast)		
Thiourea (Very fast)		R = Alkyl, Phenyl
Benzothiazole Sulfonamide (Fast – Delayed cure)		R = H, Alkyl R = Phenyl
Isopropylxanthate (Ultrafast)		$Me^{n+} = Zn^{2+}, Na^{+}$

2.3.1.2 Activators for Sulfur Vulcanization

In general sulfur vulcanization systems consist of rubber, sulfur accelerator, metal oxide and fatty acid, where ever the last two ingredients are the activator. They are necessary rubber process additives that not only activate vulcanization furthermore improve the effectiveness of sulfur primarily based vulcanize systems. In fact, most organic accelerators need the addition of associate organic activator to achieve the desired cure and end-use properties. The typical activator is zinc fatty acid ester that is usually formed in-situ by reaction of fatty acid with zinc oxide. The general fatty acids are stearic, lauric, palmitic, oleic and naphthenic acid. The fatty acid dissolves the zinc and forms the catalyst. The zinc oxide may additionally work as a filler or white colorant in rubber compounds whereas the fatty acid enhances filler incorporation and dispersion by decreasing interfacial tension and wetting the oxide particles. The adding of activators within the mixture along secondary alkaline accelerators also let in a more controlled onset of vulcanization[36].

The mechanism of zinc catalyzed sulfur cure is extremely complicated and is usually not absolutely understood[36]. The predominate catalyst is zinc since the fatty acid functions as a dissolving agent for the zinc that forms a complex including sulfur within the accelerator-polysulfide and is covalently bonded to sulfur atoms within the accelerator molecule as shown in Figure 2.7. Both the solubility associated reactivity will enlarge if the zinc coordinates with an amine or amide, such as sulfenamide. The chelated amines enlarge the nucleophilicity concerning the sulfur within the polysulfide complex then thereby extend the reaction rate regarding precursor formation. The position of zinc within the accelerator complex influences each the reaction path and the production distribution. The accelerator complex performs a very necessary role of both the insertion of sulfur atoms within the complex and the formation of initial polysulfidic crosslinks. For this case with alternative catalysts, exceptional small quantities of solubilized zinc are required to initiate and speed up the cure process[36].

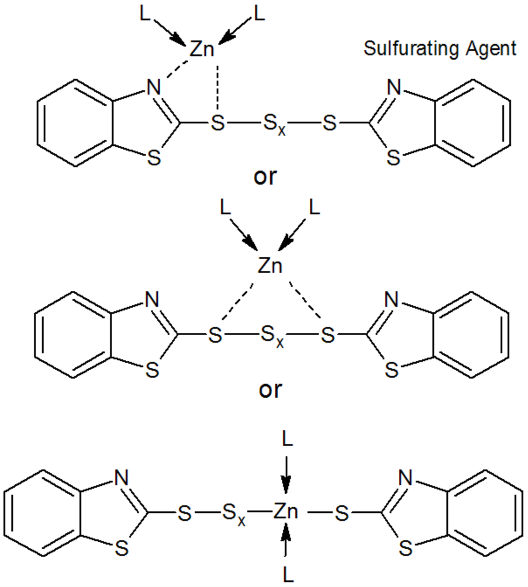


Figure 2.7 The complex forms of sulfur with the accelerator

2.3.2 Peroxide Vulcanization

Peroxide vulcanization[38-40] results in a rubber network that the polymer chains are joined together by covalent carbon-carbon bonds. Peroxide vulcanizates have higher thermal properties, such as heat ageing and compression set than the sulfur vulcanizates[38]. Moreover, peroxide vulcanization can be taken place in both unsaturated and saturated polymers. Some mechanical properties of peroxide vulcanization are lower than sulfur vulcanization, for example tensile strength, dynamic properties. Another serious problem of peroxide vulcanization is the shortage of sufficient scorch time (the time before vulcanization starts, it is importance to control the vulcanization reaction). The scorch safety is the scorch time that allows to process material before it starts to vulcanize[39]. The reaction of peroxide vulcanization is shown below[39].

$$\mathrm{R\text{-}O\text{-}O\text{-}R} \longrightarrow 2\ (\mathrm{R\text{-}O})^*$$

Figure 2.8 The decomposition of peroxide

Peroxide vulcanization is radical reactions, involve three steps initiation, propagation and termination. Figure 2.8 shows the initiation step. This step is induced by homolytic decomposition of a peroxide species. Normally, the peroxide decomposition is activated by heat[39].

In general, the temperature and time of the vulcanization reaction are associated with the half-life time of the peroxide. The peroxide half-life time ($t_{1/2}$) is outline by the time needed to decompose one half of the initial quantity of peroxide at a precise reaction temperature. In normal, the increase of 10 °C of temperature, the peroxides half-life time drops to about 1/3. Typically, the rubber is vulcanized for the equivalent of a minimum of five half-life times to make sure that only a trace of unreacted peroxide remains. This is because the residual peroxide may lead to oxidation, chain scission or formation of further crosslinks control by temperature throughout product service.

Figure 2.9 shows the propagation step[39]. It can be seen that the alkoxy radical abstracts a hydrogen atom from a polymer chain. This reaction is bimolecular because it has the alkoxy radical and the polymer chain. Nonetheless, it is not a second order reaction since the amount of hydrogen atoms is significantly massive and therefore their concentration does not vary considerably as the reaction proceeds. At that time, the kinetics of the reaction are determined only by the concentration of alkoxy radicals due to the propagation step which is a first order reaction. The concentration of alkoxy radicals is extremely low, since they are terribly energetic species. Consequently, the extent of polymer radicals formed is directly proportional to the number of peroxides consumed.

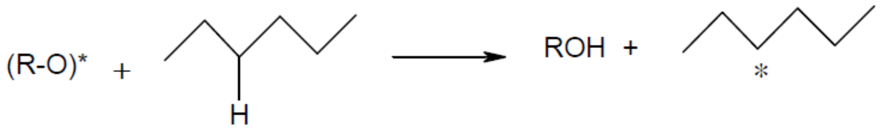


Figure 2.9 Propagation by hydrogen abstraction from the polymer chain

The alkoxy radical may also add to the unsaturation, even though that occurs to a less extent than hydrogen detraction. An alkoxy radical detract a hydrogen atom not merely from the polymer chain but also from any other usable source. Figure 2.10 shows the order of lability of hydrogen atoms[39].

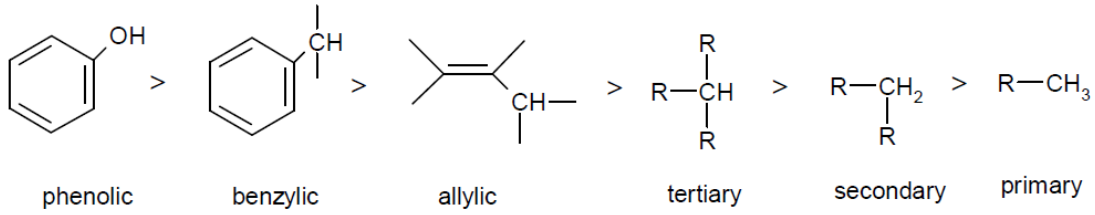


Figure 2.10 Order of hydrogen lability

Because of the high lability of allylic hydrogen and benzylic atoms. The aromatic oils, that contain an extensive concentration of both kind of hydrogen atoms, should be prevented within rubber compounding to keep away from the destruction of peroxide radicals from their part. Paraffinic plasticizers take alkoxy radicals less than aromatic and naphthenic oils. The alkoxy radical reacting with ethylenic unsaturation can also initiate polymerization. Due to of polyfunctional reactive additives (co-agents) are usually added to the formulation as vary vulcanizing characteristics. Lastly, two radicals on adjacent polymer chains couple to form a carbon-carbon covalent crosslink in the termination step[39] (Figure 2.11).

Figure 2.11 Termination by coupling of two polymer radicals

According to this reaction, two polymer radicals form one crosslink. Theoretically, one crosslink should be obtained from one peroxide molecule. However, the efficiency is usually lower than one due to the prevalence of side reactions. For example, if oxygen molecules are present throughout the vulcanization they will couple to the radical formed on the polymer backbone to yield a hydroperoxide radical, that results in polymer degradation rather than a crosslink. Due to this, peroxide vulcanization should be performed within the absence of oxygen. The other side reactions that can occur to the polymer radical are chain scission and disproportionation[39] (Figures 2.12 and Figure 2.13). These reactions are appreciated through the presence of tertiary radicals and they contribute to reducing of the peroxide efficiency.

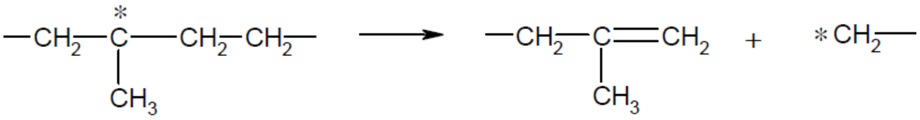


Figure 2.12 Chain scission in the polymer backbone

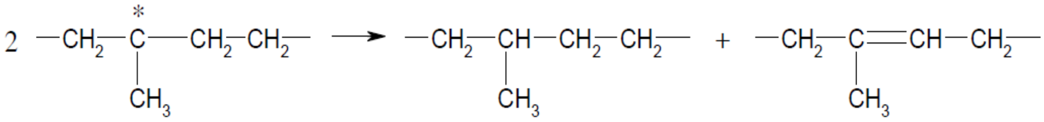


Figure 2.13 Disproportionation of the polymer radical

Moreover, there are side reactions that can influence the peroxide vulcanization in a negative manner, for example metal catalyzed decomposition of the peroxide, oxygenation, dehydrohalogenation and radical transfer. In addition, the presence of acidic substances, which causes heterolytic or ionic decomposition of the peroxide molecule. Therefore, no radicals are formed thus crosslinking does not occur. Accordingly, the presence of some fillers being acidic can reduce the crosslinking efficiency. For this reason, the fillers used of peroxide vulcanization might also not be acidic on nature. In conclusion, a helpful selection of the formulation ingredients is crucial importance in order to decrease the prevalence of the negative side reactions and increase the efficiency of crosslinking.

2.4 Literature Reviews

2.4.1 Bi-functional Vulcanizing Agent for ENR

Pire *et al.* found that the dodecanedioic acid (DA) can be used as a crosslinking agent for ENR[12-15]. However, the use of DA as a crosslinking agent required a least 3 hours at 180 °C to complete the reaction. This long reaction time significantly caused the thermal degradation of rubber. Later Pire *et al*. found that the vulcanization of ENR with DA can be tremendously accelerated by 1,2-dimethylimidazole (DMI). It was proposed that the crosslinking took place via ring opening of epoxide group by DA[13] as shown in Figure 2.14. Although the result from this study revealed that this simple crosslink system (DA with the presence of DMI) can efficiently crosslink ENR, the mechanical properties of the DA crosslinked ENR is still low when compared with the sulfur crosslinked ENR.

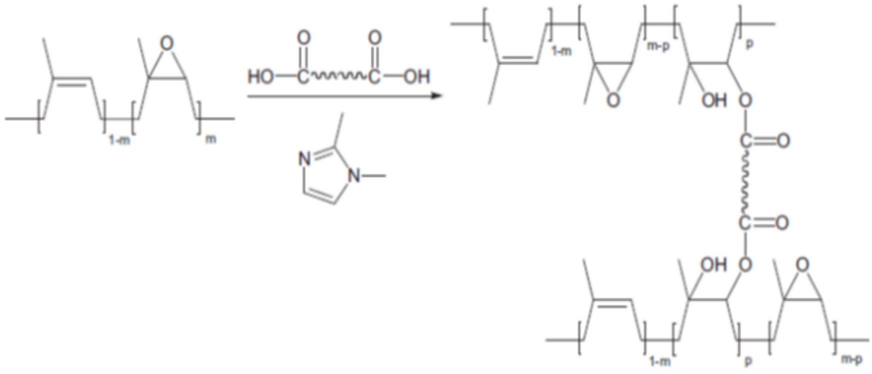


Figure 2.14 Crosslinking of ENR with DA in the presence of DMI

Yoksan[16] investigated the suitable non-sulfur crosslinking system for ENR. Two non-sulfur crosslinking systems studied were diamine catalyzed by bisphenol A and anhydride catalyzed by imidazole. The result showed that the crosslinking efficiency of the anhydride/imidazole crosslink system was higher than that of the diamine/bisphenol A crosslink system. However, when comparing with conventional sulfur crosslinking, the result showed that for adhesive application the sulfur cured ENR adhesive gave the higher tensile strength than the anhydride cured ENR.

From literature survey, up to now, the development of non-sulfur crosslinking system for ENR still does not give the non-sulfur cured ENR with higher strength than the sulfur cured ENR.

Besides searching new crosslinking agents that give the modified NR such as ENR with superior properties, many researches are also interested in the development of thermoreversible crosslinking system. As mentioned above, conventional crosslinking systems lead to the formation of thermoset. This means the obtained crosslinked rubbers cannot be reused or recycled. Therefore, the study of thermoreversible crosslinking rubber is the urgent issue to save the environment. The key to achieve the thermoreverisble crosslinking is the formation of bonding weakening at elevated temperatures such as hydrogen bonding.

2.4.2 Thermoreversible Crosslinking of Rubber

Thermoreversible crosslinking of polyisoprene rubber (TRC-IR) was prepared by Chino *et al.* [17-19]. The preparation of TRC-IR started from the grafting of polyisoprene rubber (IR) with maleic anhydride (MA) through a kneading process at 50 rpm at 210 °C for 60 min. Then, the maleic anhydride grafted polyisoprene rubber were mixed with thermoreversible crosslinking agent, 3-amino-1,2,4-triazole (ATA) by kneading at 50 rpm at 80 °C for 30 min. The vulcanization took place by heating the maleic anhydride grafted polyisoprene rubber/ATA compounds at 160 °C for 20 min. Figure 2.15 shows the synthesis path of TRC-IR. Due to the presence of hydrogen-bonding moiety (amide triazole-carboxylic acid) generated by the addition reaction of ATA and acid anhydride, the crosslinking took place by strong hydrogen bonds between the amide triazole-carboxylic acid units of rubber chains as shown in Figure 2.16. Due to the higher mechanical properties than the uncured IR and the presence of a second endothermic transition around 80 °C in the DSC curve indicating the cleavage of the hydrogen bonding, it was implied that there was strong crosslinking amongst the modified IR chains. Moreover, the study showed that the TRC-IR can be re-molded and repeated more than 10 times without significantly changing its mechanical properties.

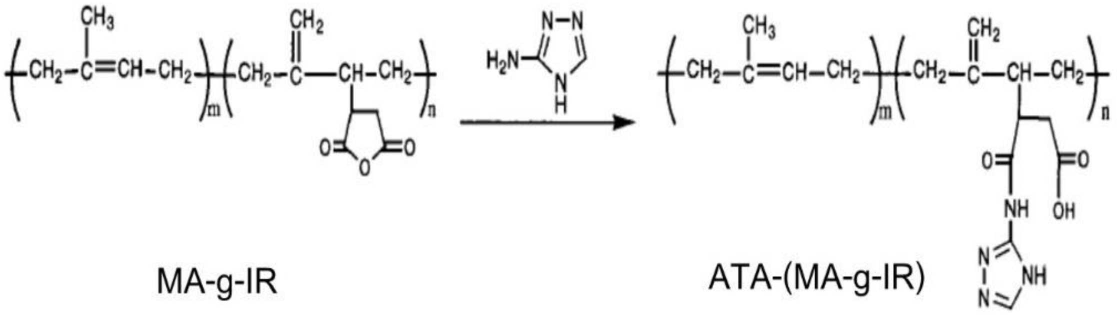


Figure 2.15 Synthesis of TRC-IR

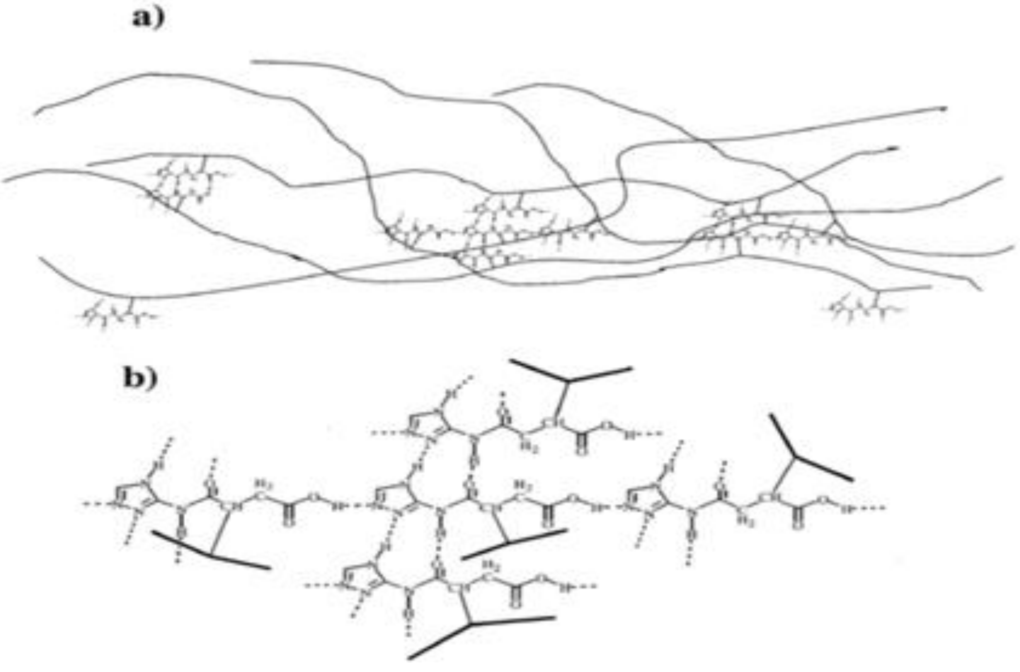


Figure 2.16 a*)* A speculated model of the structure of TRC rubber. b*)* A speculated model of the crosslinking moiety of TRC rubber

Chino[19] further investigated the physical and mechanical properties of thermoreversible crosslinking ethylene propylene rubber (TRC-EPM). The mechanical properties of TRC-EPM were compared with those of the sulfur cured EPDM and the PP/EPDM thermoplastic vulcanizate (TPV) as shown in Table 2.3.

Table 2.3 Mechanical properties and recyclability of TRC-EPM, vulcanized EPDM and TPV

Rubber	**TRC-EPM**	**Vulcanized EPDM**	**TPV (PP/EPDM)**
Hardness	73	48	72
100% modulus (MPa)	2.4	1.0	3.3
Tensile strength (MPa)	9.3	1.9	7.1
Elongation at break (%)	660	255	480
Compression Set (%)	38	12	34
Recyclability	OK	NG	OK

From the above result, it can be seen that the mechanical properties of TRC-EPM were sufficiently high for technical applications. Tensile strength of TRC-EPM was higher than that of the sulfur cured EPDM and the TPV. However, the compress set of TRC-EPM was worse than that of the sulfur cured EPDM but was almost the same as that of TPV. This suggested that there was a rearrangement of the hydrogen bonding. From small angle X-ray scattering analysis of TRC-EPM, it revealed that there was the existence of an aggregate structure with domains of 5.2 nm. These aggregate structures are supposed to act as the crosslinking domains. Since TRC-EPM had small crosslinking domains and did not include thermoplastic polymer[19] as shown in Figure 2.17. The general properties were similar to those vulcanized rubber.

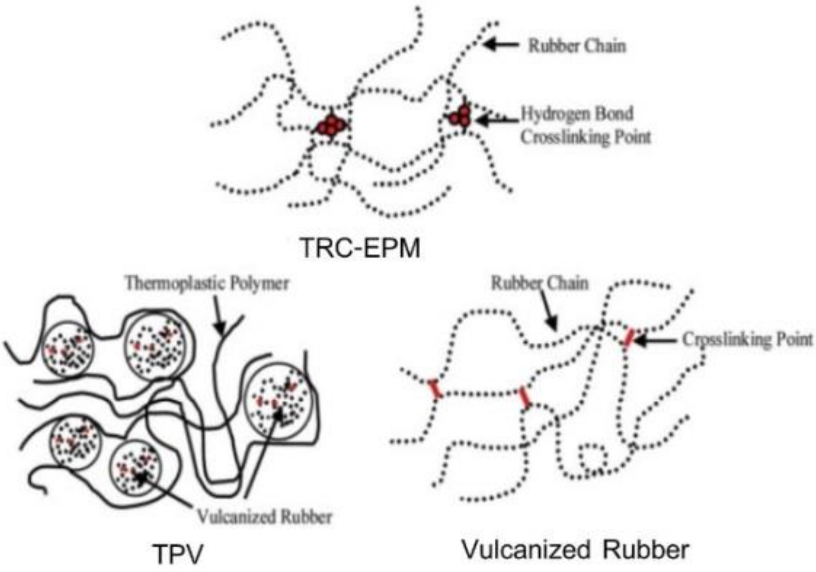


Figure 2.17 A speculated model of the structure of TRC-EPM, TPV and vulcanized rubber

Sun *et al.*[22] also prepared the thermoreversible crosslinking of maleic anhydride grafted ethylene/propylene copolymers (MA-g-EPM) but via a reaction with primary alkylamines of different length with an equimolar amount to obtain the amide-acid giving only hydrogen bonding or an excess to obtain the amide-salt giving a combination of hydrogen bonding and ionic interactions as shown in Figure 2.18. Small-angle X-ray scattering experiments showed the presence of microphase-separated aggregates for both the starting MA-g-EPM and alkylamide-acids and alkylamide-salts. This can be inferred that there were physical crosslinks holding rubber chains together. The mechanical properties were improved by converting MA-g-EPM to the amide-acids due to hydrogen bonding and even further by converting the amide-acids to amide-salts due to additional ionic interactions besides hydrogen bonding. From tensile testing, it was found that better tensile properties and elasticity were observed for the octadecylamine (amine with the longest length, C18), which was explained by packing of the long alkyl tails in a crystalline-like order. The obtained sample could be remolded at 80 °C into homogeneous films for several times, indicating that the (physical) crosslinking were truly reversible. However, it was found that there was the possibility to form irreversible imide for all amide-acids and amide-salts at high temperatures (180 °C), resulting in disappearance of the aggregates and, hence a dramatic decrease in mechanical properties.

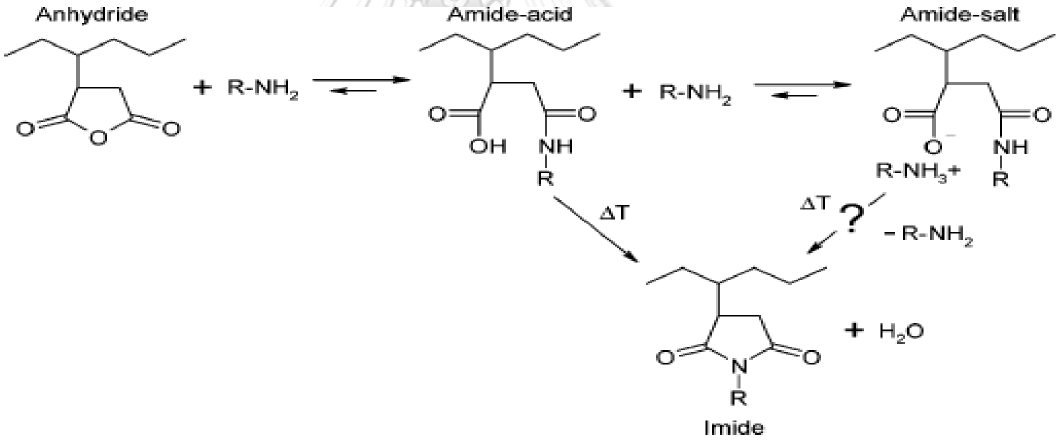


Figure 2.18 Reaction scheme for the Modification of MA-g-EPM with primary amines

Li *et al.*[20] prepared the thermoreversible crosslinking maleic anhydride grafted butyl rubber (TRC-IIR) with ATA catalyzed by tetrabutyl ammonium bromide using a solution method. The hydrogen bonding arrays occurred via the reaction between the obtained amide triazole-caroxylic acid groups. The physical crosslinks in the MA-g-IIR is significantly tightened and strengthened after introducing multiple hydrogen bonds. Even the TRC- IIR was remolded more than 3 times. Moreover, its tensile strength was still much higher than that of the MA-g-IIR. The reprocessability of the thermoreversible crosslink IIR was due to the thermoreversibility of hydrogen bond at elevated temperature, while the maintenace of tensile properties was due to the recovery of hydrogen bond during cooling.

Besides the formation of thermoreversible crosslinking via hydrogen bonding and ionic bonding, some researches also prepared thermoreversible crosslinking rubber via the covalent crosslinks. Mee *et al.*[23] synthesized the thermoreversible crosslinking MA-g-EPM using the equilibrium reaction with diols as shown in Figure 2.19. The reaction of anhydrides with alcohols formed the covalent hemi-ester crosslinks, while an equilibrium shifted at elevated temperatures may result in their removal. High conversions to hemi-ester are obtained at low temperature, whereas conversions are low at high temperature. P-toluenesulfonic acid was used as a catalyst. MA-g-EPM and all diol crosslinked MA-g-EPM showed the microphase-separated aggregates acting as physical crosslinks. The covalent crosslinks were only formed within the aggregates. The mechanical properties of MA-g-EPM were significantly improved upon increasing level of crosslinking, whereas the type of diol has less influence. The reprocessing of covalent crosslinking MA-g-EPM occurred via compression molding at temperature above 175 °C. It was proposed that the reprocessability did not originate from an equilibrium shift, but from a dynamic exchange between crosslinked and non-crosslinked functional groups, which allowed crosslinks to disconnect and the corresponding chain segments to diffuse between aggregates.

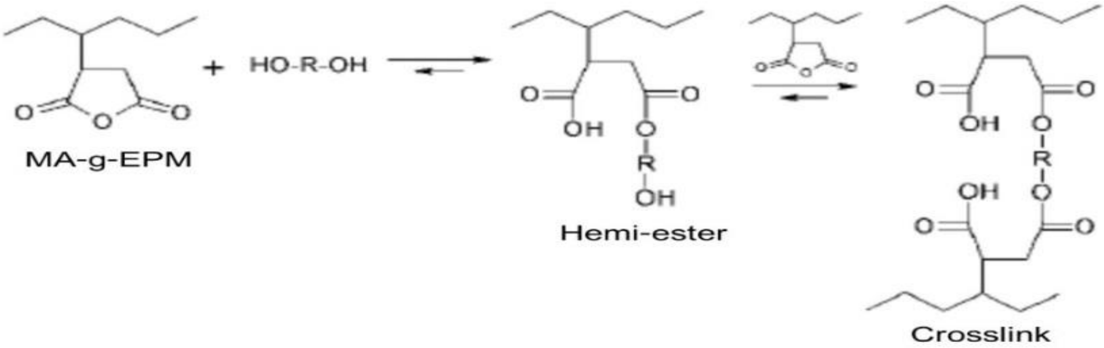


Figure 2.19 Reaction scheme for the crosslinking of MA-g-EPM with diols

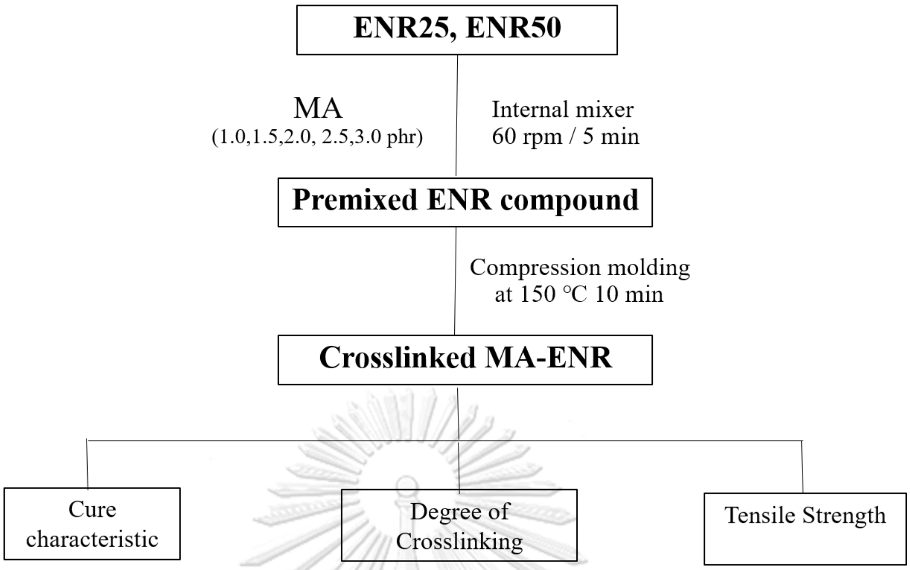
Mee *et al.* [24] further studied to improve the properties of the thermorevrsible crosslinking MA-g-EPM. Diamines and amino-alcohols were used as covalent crosslinkers. Covalent crosslinkings were formed via the equilibrium reaction of the grafted anhydride groups with di-functional crosslinkers containing combinations of primary (1°) and secondary (2°) amines and alcohols, while a shift of the equilibrium at elevated temperatures may result in their removal. The crosslinking of MA-g-EPM contained two 2° amine groups (2°- 2°) and 2° amine and alcohol groups (2°-OH) are repeatedly processable via compression molding without chemical changes. It was reported that the 2°-2° and 2°-OH crosslinking MA-g-EPM have higher level of crosslinking after remolding than the diol-crosslinking MA-g-EPM, which results in significant differences in rubber properties.

CHAPTER 3

METHODOLOGY

This study was aimed to develop a novel crosslinking system for ENR and NR. The first part was to investigate the possibility to use maleic anhydride (MA) as a novel di-functional molecule for crosslinking ENR. Two types of ENR including ENR25 and ENR50 were used here. For the second part, it was about the preparation of thermoreversibly crosslinking of NR. For this part, NR was initially grafted with maleic anhydride (MA) to form maleated NR or MNR. Then, the obtained MNR was mixed with thermoreversible crosslinking agent. Two reagents including glycerol and diethylene glycol were tested in order to use as a crosslinking agent. The overall scope of this study is summarized as a flowchart in Figure 3.1.

Part I Preparation of ENR crosslinked with MA



Part II Preparation of thermoreversible crosslinking of NR

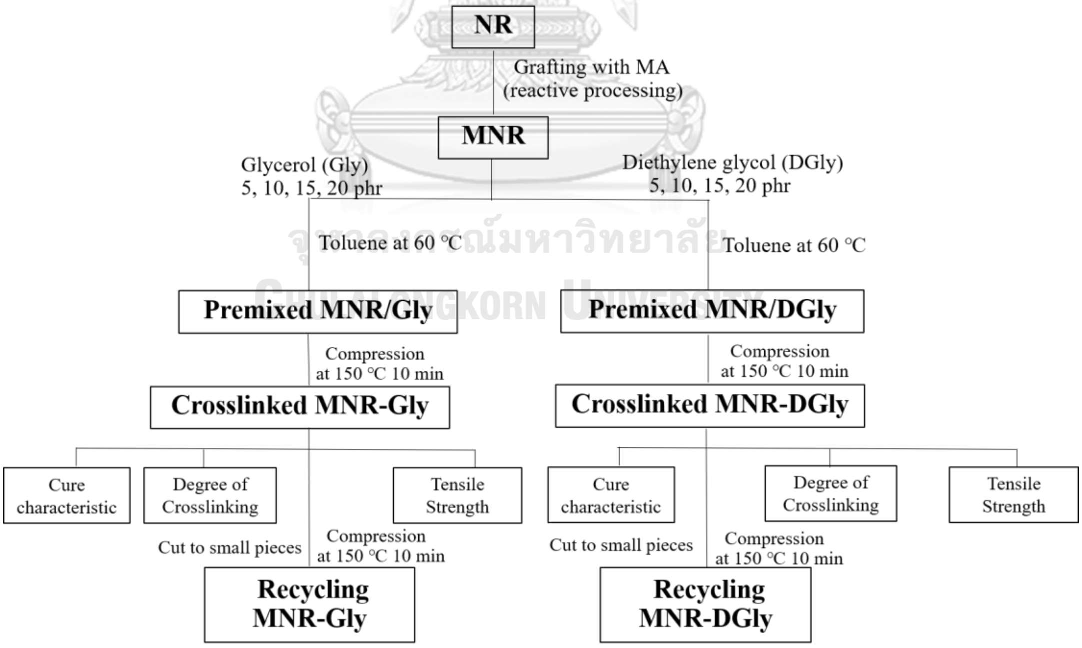


Figure 3.1 Overall scope of this study

3.1 Materials

All materials used in this research and their sources were listed in Table 3.1

Table 3.1 Materials and their sources

Material	Grade	Source
Natural rubber (NR)	STR 5L	Sakdaroongreungkij (Local supplier)
Epoxidized natural rubber 25 mol% epoxide groups	ENR25	San-Thap (Local supplier)
Epoxidized natural rubber 50 mol% epoxide groups	ENR50	San-Thap (Local supplier)
Maleic anhydride (MA)	Analytical Grade	Fluka Analytical
Toluene	Commercial Grade	RCI Labscan
Acetone	Commercial Grade	Acetone Comm
Glycerol (Gly)	Analytical Grade	RCI Labscan
Diethylene glycol (DGly)	Analytical Grade	Loba Chemie
Potassium hydroxide (KOH)	Analytical Grade	Loba Chemie
Methanol	Analytical Grade	Loba Chemie
Benzyl alcohol	Analytical Grade	Loba Chemie
Phenolphthalein	Analytical Grade	Riedel-Dehaen

3.2 Equipment and Instruments

The list of equipment/instruments (model and manufactures) used in the study were listed in Table 3.2.

Table 3.2 List of equipment/instruments

Equipment/Instruments	Model and Manufactures
Internal mixer	MX500-D75L90 Chareon TUT co., ltd.
Two- roll mill	Lab Tech engineering company ltd.
Compression molding	Lab Tech engineering company ltd.
Fourier Transform-Infrared Spectroscopy (FT-IR)	IR Prestige-21 Shimadzu
Thermogravimetrical analysis (TGA)	TGA Mettler -Toledo
Moving Die rheology (MDR)	Rheotech MD Moving Die Rheometer
Universal testing machine	Instron model 5564
Nuclear Magnetic Resonance Spectrometer (^{1}H-NMR)	JEOL AL-400 spectrometer
Differential Scanning Calorimetry (DSC)	Thermo plus EVO DSC 8230 Rigaku instrument

3.3 Preparation and Characterization of ENR crosslinked with MA

3.3.1 Preparation of ENR Crosslinked with MA

ENR was mixed with different amount of MA as listed in Table 3.3 using an internal mixer (as shown in Figure 3.2). Firstly, 200 g of ENR was masticated in a mixer with a maximum loading capacity of 500 cc at room temperature and at 60 rpm rotor speed for 2 min. After that, MA with various contents and 70 phr of $CaCO_3$ were added to the masticated rubber and mixed together for 5 min. The compound was dumped and then sheeted off using a two-roll mill. The obtained compounds were crosslinked in a compression molding (as shown in Figure 3.3) at a specific condition that was determined from FTIR spectroscopy. The crosslinked compounds were shown in Figure 3.4. It was noted that a smooth rubber sheet cannot be obtained from all ENR50 cured with MA.

Figure 3.2 Internal mixer (MX500-D75L90 Chareon TUT co., ltd.)

Figure 3.3 Compression molding (Lab Tech engineering company ltd.*)*

3.3.2 Characterization of ENR Crosslinked with MA

- Cure Characteristic

In this study, the optimum curing condition was investigated using a FT-IR spectroscopy (IR Prestige-21 Shimadzu as shown in Figure 3.5) equipped with a variable temperature cell holder. The sample for a measurement was prepared by dissolving ENR in toluene at room temperature. After that, MA at various contents were added into the homogenous ENR solution. To obtain thin films of rubber on KBr pellets, the solutions of pure ENR and ENR mixed with MA at various contents were dropped on KBr pellet. Then solvent was evaporated by a hair dryer. FT-IR spectrum of the pure ENR and MA/ENR film was recorded at 25 °C. For the MA/ENR film, after the spectrum at 25 °C was obtained, the samples were heated to 150, 160 and 170 °C and held for a certain time, then the spectrum of the heated MA/ENR film were recorded at the heating stage.

ENR 1.0MA-ENR25

1.5MA-ENR25 2.0MA-ENR25

2.5MA-ENR25 3.0MA-ENR25

1.0 MA-ENR50 2.5MA-ENR50

Figure 3.4 Overview pictures of ENR crosslinked with MA

Figure 3.5 Fourier transform-infrared spectrometer (IR Prestige-21 Shimadzu)

Table 3.3 Formulation of ENR mixed with different amount of MA

Sample Name	Amount of MA (phr)
1.0MA-ENR25	1.0
1.5MA-ENR25	1.5
2.0MA-ENR25	2.0
2.5MA-ENR25	2.5
3.0MA-ENR25	3.0
1.0MA-ENR50	1.0
1.5MA-ENR50	1.5
2.0MA-ENR50	2.0
2.5MA-ENR50	2.5
3.0MA-ENR50	3.0

Moreover, the cure characteristic of ENR crosslinked with MA was also investigated using a Rheotech MD Moving Die Rheometer as shown in Figure 3.6. A 5 g of sample was sandwiched with two cellophane sheets to avoid the tackiness of sample with die. The measurement was carried out at 150 °C.

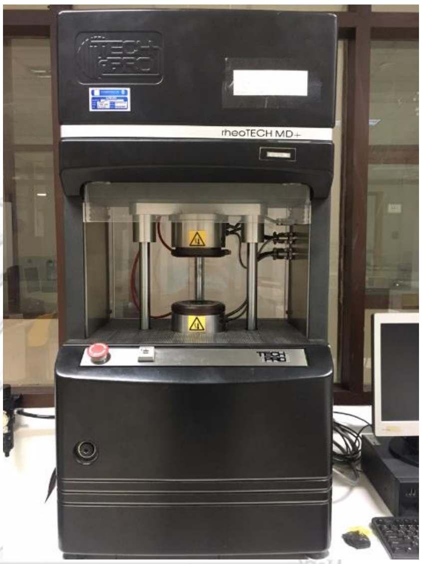


Figure 3.6 Moving Die rheometer (Rheotech MD Moving Die Rheometer)

- *Degree of Crosslinking*

The degree of crosslinking can be referred from the swelling index. Qualitatively, it is was inversely proportional to the swelling index. The cured MA-ENR samples about 0.25 gram were immersed in toluene for 7 days. Swelling index (%) was calculated as followed:

$$\text{Swelling index (\%)} = \frac{\mathrm{W}_1}{\mathrm{W}_0} \times 100$$

where W_1 and W_0 are the weight of swollen sample and the weight of dried sample respectively.

- *Thermal Degradation Behavior*

Thermal decomposition of rubber before and after crosslinking with MA was determined by a TGA Mettler -Toledo as shown in Figure 3.7. The samples were heated under nitrogen atmosphere at a heating rate of 10 °C/min from 50 to 1000 °C.

Figure 3.7 Thermogravimetric analysis (TGA Mettler -Toledo)

- *Tensile Properties*

Tensile testing was carried out by a universal testing machine Instron model 5564 (Figure 3.8) in accordance with ASTM D412. Crosshead speed was 500 mm/min. For each sample, five specimens were tested. Modulus at 100% and 300% elongation (M_{100} and M_{300}), tensile strength (TS) and elongation at break (EB) were reported.

Figure 3.8 Universal testing machine (Instron model 5564)

3.4 Preparation and Characterization of Thermoreversible Crosslinking NR

3.4.1 Preparation of Thermoreversible Crosslinking NR

As mentioned earlier to prepare thermoreversible crosslinking NR, it is necessary to initially modify NR with maleic anhydride. Then, the obtained maleated NR or MNR reacts with crosslinking agents to form the NR crosslinking network. Therefore, the preparation step is divided into to two parts.

3.4.1.1 Preparation of Maleated NR

The MNR was prepared by a reactive processing method without the presence of initiator. 200 g of NR was masticated for 3, 5 and 7 min in an internal mixer at room temperature with 60 rpm rotor speed. After that, MA at various quantities (10, 12 and 14 phr) was added to the compound and mixed together for 10, 15 and 20 min at 140, 150 and 160 °C. The MA was grafted onto NR by the shear of screw rotor via free radical mechanism. Formulation of different MNR samples are tabulated in Table 3.4. Before carrying out to the next step, the unreacted MA was removed by dissolving the obtained MNR in toluene and then coagulated in acetone. The sample is named as xMNR when the “x” is a number indicating the amount of added MA. As for example, 14MNR indicates NR mixing with 14 phr of MA.

Table 3.4 Formulation of MNR

Sample Name	**Amount of MA (phr)**
10MNR	10
12MNR	12
14MNR	14

3.4.1.2 Preparation of Thermoreversible Crosslinking MNR

Two thermoreversible crosslinking agents including glycerol (Gly) and diethylene glycol (DGly) were used in this study. A 50 g of washed MNR from the previous part was dissolved in toluene at 60 °C stirred until the homogenous solution was obtained. After that 5, 10, 15, 20 phr of crosslinking agent were added into the solution and then stirred for 2 hours. In the final step, the solution was poured into a glass tray and evaporated at room temperature for 2 days. The formulation of MNR mixed with Gly and DGly at various contents is given in Table 3.5 and 3.6, respectively.

Table 3.5 Formulation of MNR-Gly

Sample Name	**Amounts of Glycerol (phr)**
MNR-5Gly	5
MNR-10Gly	10
MNR-15Gly	15
MNR-20Gly	20

Table 3.6 Formulation of MNR-DGly

Sample Name	**Amounts of Diethylene Glycol (phr)**
MNR-5DGly	5
MNR-10DGly	10
MNR-15DGly	15
MNR-20DGly	20

Then, the resulting film was compression molded at 150 °C for 10 min, thus forming thermoreversible covalent linkages. To study thermoreversibility of the MNR, the samples were recompression molded at 150 °C for various heating-cooling cycles.

3.4.2 Characterization of Thermoreversible Crosslinking NR

- Degree of MA grafting (%)

The % of MA grafted onto the NR molecules was determined by titration of acid groups derived from the anhydride functions with an alkaline solution. At the beginning 1.0 g of MNR was dissolved in 100 ml of toluene at boiling temperature, after that 0.2 ml of water was added to hydrolyze anhydride functions into carboxylic acid functions. Then the solution was refluxed for 2.0 h to complete the hydrolysis. The amount of carboxylic acid concentration was determined by titration with 0.025 N potassium hydroxide in methanol/ benzyl alcohol 1/9 (v/v). The indicator used was a solution of 1% phenolphthalein in methanol. The MNR was completely soluble in toluene at reflux conditions. Furthermore, precipitation was not observed during titration. The carboxylic acid concentration was converted to the MA content as follows[41]:

$$\mathrm{MA}\,(\%\mathrm{wt}) = \frac{\mathrm{N}(\mathrm{V}_1 - \mathrm{V}_0)}{2\mathrm{W}} \times 98 \times 100\%$$

where N is the concentration (mol/l) of potassium hydroxide dissolved in methanol/ benzyl alcohol. V_0 and V_1 are the volumes of the KOH used in the blank test and in the test with samples, respectively. W is the weight (g) of the MNR sample.

- *Chemical Structure of MNR and Thermoreversible crosslinking MNR*

To confirm that MA was grafted onto the NR, the chemical structure of NR before and after reacting with MA was determined by a JEOL AL-400 spectrometer (as shown in Figure 3.9). Deuterated chloroform ($CDCl_3$) was used as a solvent in the preparation of sample.

Figure 3.9 Nuclear Magnetic Resonance Spectrometer (a JEOL AL-400 spectrometer)

The FT-IR spectra of samples including pure NR, MNR, MNR premixed with Gly and DGly and the resultant crosslinked MNR were recorded on a Shimadzu IR Prestige-21 FTIR spectrometer equipped with a variable temperature cell holder. The sample was firstly dissolved in toluene and then deposited onto KBr pellets. After evaporation of toluene, a thin film was generated. Each sample was scanned for 64 times at a resolution of 4 cm^{-1} over the range of 4000-400 cm^{-1} at 25 ^{o}C. For the MNR premixed with Gly or DGly, once the sample was completely scanned at 25 ^{o}C, the sample was then heated to 150 ^{o}C and held at this temperature for 10 min and then cooled down to 25 °C. The spectrum of this crosslinked sample was recorded again at 25 °C. To investigate the change of crosslink structure during thermoreversible process, the sample was scanned at 25 °C and 150 °C for various heating-cooling cycles.

- *Degree of Crosslinking*

The degree of crosslinking was referred from the swelling index. The crosslinked samples about 0.25 gram were immersed in toluene for 7 days. Weight of dried and swollen samples were recorded. Swelling index (%) was calculated as followed:

$$\text{Swelling index (\%)} = \frac{W_1}{W_0} \times 100$$

where W_1 and W_0 are the weight of swollen sample and the weight of dried sample respectively.

- *Cure Characteristic*

Crosslinking curves were recorded with a Thermo plus EVO DSC 8230 Rigaku instrument (Differential Scanning Calorimetry, DSC). All samples were conducted at the heating-cooling rate of 5 °C /min, with the flow rate of 10 ml/min, in the temperature range from 40 - 170°C. The instrument was calibrated using indium as a standard. The samples of about 5 mg were placed in aluminum pans. After the first heating run, the samples were cooled down, and subsequently heated again with same rate (second heating run). After each measurement, the samples were held for 10 min at a constant (minimal and maximal) temperature.

- *Tensile Properties*

Tensile properties were determined using a universal testing machine Instron model 5564, in accordance with ASTM D412. Crosshead speed was 500 mm/minute. For each sample, five specimens were tested. Tensile properties including modulus at 100% elongation (M_{100}), modulus at 300% elongation (M_{300}), tensile strength (TS) and elongation at break (EB) were recorded.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Crosslinking of Epoxidized Natural Rubber with Maleic Anhydride

Crosslinking is a reaction that bonds one rubber chain to another one, thus forming a three-dimension network. Therefore, this reaction converts rubber which initially is a thermoplastic to a thermoset. In order to confirm that maleic anhydride (MA) can be used as a crosslinking agent for epoxidized natural rubber (ENR), several testing were carried out and the results were given here. Both commercial ENRs including ENR25 and ENR50 were used here. Unfortunately, it was found that the ENR50 cannot formed a smooth rubber sheet (Figure 3.4). Therefore, some of their properties cannot be evaluated.

4.1.1 Chemical Structure of ENR25 Crosslinked with MA

FT-IR spectra of ENR25 premixed with MA without heating and ENR25 crosslinked with MA were compared with that of uncrosslinked ENR25 (without MA) in Figure 4.1. Initially, the main characteristic peak of ENR25 was found at 870 cm^{-1} referring to the stretching of asymmettric oxirane ring. Additionally, after mixing ENR with MA without heating, the peaks at 1790 cm^{-1} and 1835 cm^{-1} emerged. These two peaks represented the C=O stretching of succinic anhydride rings. Once the ENR25 premixed with MA was heated, there were two peaks at 1735 cm^{-1} and 1710 cm^{-1} newly formed. These newly formed peaks represented the C=O stretching of ester and carboxyl group indicating the reaction between ENR and MA occurred via the ring opening of MA. The peak assignments of uncrosslinked ENR25 (without MA), ENR25 premixed with MA without heating and ENR25 crosslinked with MA are listed in Table 4.1.

Table 4.1 FT-IR peak assignments of uncrosslinked ENR25 (without MA), ENR25 premixed with MA without heating and ENR25 crosslinked with MA.

Peak designation	**Wave number (cm^{-1})**
Uncrosslinked ENR25 (without MA)	
C=C, bending	835
C-O-C, asymmetric stretching	870
C-O-C, symmetric stretching	1247
-CH-, deformations	1377
-CH_2-, deformations	1450
-CH_2-, symmetric stretching	2860
-CH_2-, asymmetric stretching	2926
-CH_3-, stretching	2960
$R_1R_2C{=}CHR_3$	3036
ENR25 premixed with MA without heating	
C=C, in anhydride	698
C=O, symmetric stretching (stronger) in anhydride	1790
C=O, asymmetric stretching (weaker) in anhydride	1835
ENR25 crosslinked with MA	
C=O, stretching in carboxylic acid	1710
C=O, stretching in ester	1735

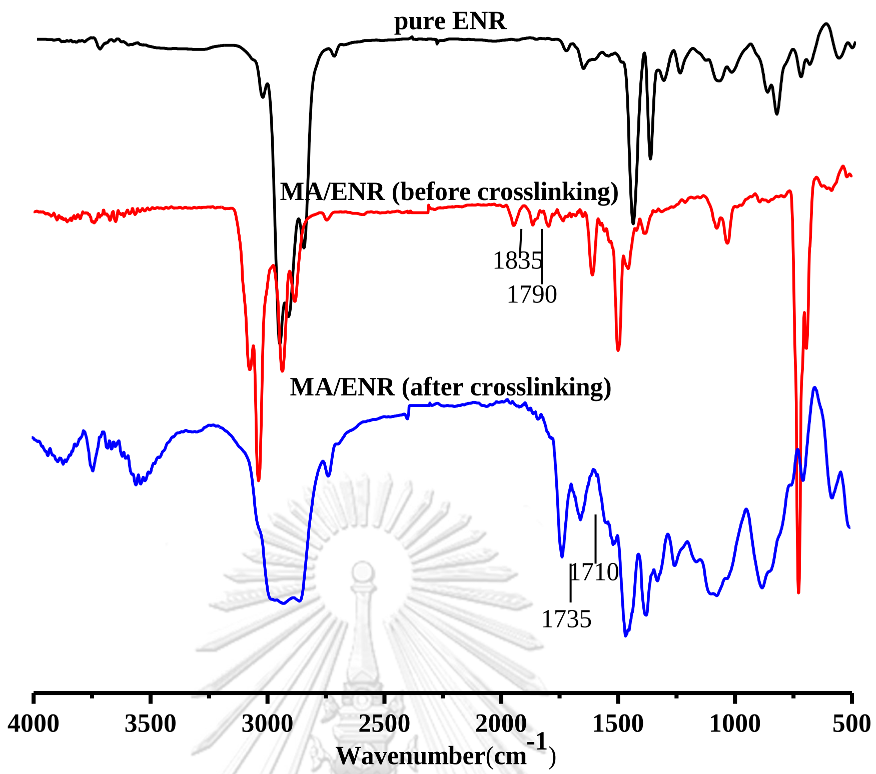


Figure 4.1 FT-IR spectra of uncrosslinked ENR25 (without MA), ENR25 premixed with MA without heating and ENR25 crosslinked with MA

4.1.2 Proposed Mechanism of ENR Crosslinked with MA

ENR is consisted of two active sites including C=C and epoxide ring along the rubber chains. Therefore, the crosslinking of ENR by MA can occur by the reaction between C=C in the rubber chain or the ring opening on the oxirane ring of the ENR. However, to react with C=C, the peroxide catalyst is needed. Moreover, from the above FT-IR spectra, the C=O stretching of ester and carboxyl group were formed. Therefore, it was believed here that the crosslinking of ENR was introduced by a ring-opening of the oxirane ring with the succinic anhydride ring of MA without catalyst. This reaction produced large percent of ester linkages[42, 43]. The possible crosslinking reaction was proposed in the Figure 4.2. Due to the high sensitivity of MA toward the moisture in air, the moisture might open the succinic anhydride ring of MA, leading to the formation of diacid compound[44]. Then, the hydroxyl group of diacids reacted with the epoxide groups along the rubber chains, thus causing a ring opening of epoxide groups and producing the ester linkages between the rubber chains[7].

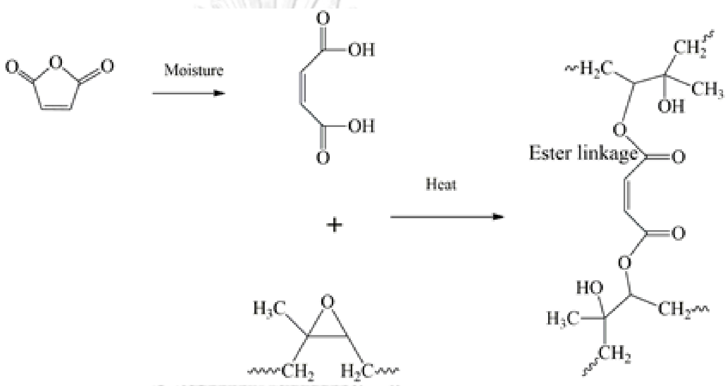


Figure 4.2 The proposed crosslinking reaction of ENR with MA

4.1.3 Swelling Index (%) of ENR Crosslinked with MA

Due to the converting from thermoplastic to thermoset, the crosslinked rubber will just only swell in the solvent. Consequently, the degree of crosslink density is reversely proportion to the swelling index. To confirm that ENR was crosslinked by MA, the swelling index (%) of the crosslinked MA-ENR was determined. The effect of MA loading on degree of swelling are represented in Table 4.2. The "number" in front of MA indicated the loading amount in phr.

Table 4.2 Swelling index (%) of the uncrosslinked ENRs and ENRs crosslinked with different amounts of MA

Sample	**Swelling Index (%)**
ENR25	527±16
ENR50	477±7
1.0MA-ENR25	439±7
1.5MA-ENR25	389±12
2.0MA-ENR25	354±6
2.5MA-ENR25	293±4
3.0MA-ENR25	248±13
1.0MA-ENR50	215±13
1.5MA-ENR50	186±9
2.0MA-ENR50	158±11
2.5MA-ENR50	133±12
3.0MA-ENR50	103±12

Initially, it was observed that in the absence of MA the ENR25 and ENR50 also were not dissolved in toluene. There were two possibilities for this. Firstly, the crosslinking was taken place due to the shear force during mixing ENR with $CaCO_3$. Rubber is a polymer that has long molecular chains. Therefore, during mixing high shear forces were needed to permit the flow of rubber, thus causing the mechanical breakdown of rubber chain. Therefore, shorter chains with free radicals at their ends were formed. The initial radicals can abstract hydrogen atom from both intramolecular and intermolecular chains, forming radical along the rubber chain. When these radicals react with oxygen, it can lead to oxidative breakdown of the rubber chain. On the other hand, these radical also can recombine. As a consequence of chain recombining, the crosslink was formed. The second reason that caused the ENR in the absence of MA not to dissolve in toluene was the physicsorption of rubber chain onto the surface of $CaCO_3$. This also inhibits the dissolving of ENR in toluene. However, the crosslinking of ENR by MA can be indicated by decreasing in swelling index. As seen in Figure 4.3, all samples reacting with MA had lower swelling index than their original ones. This can be confirmed that the crosslinking was taken place.

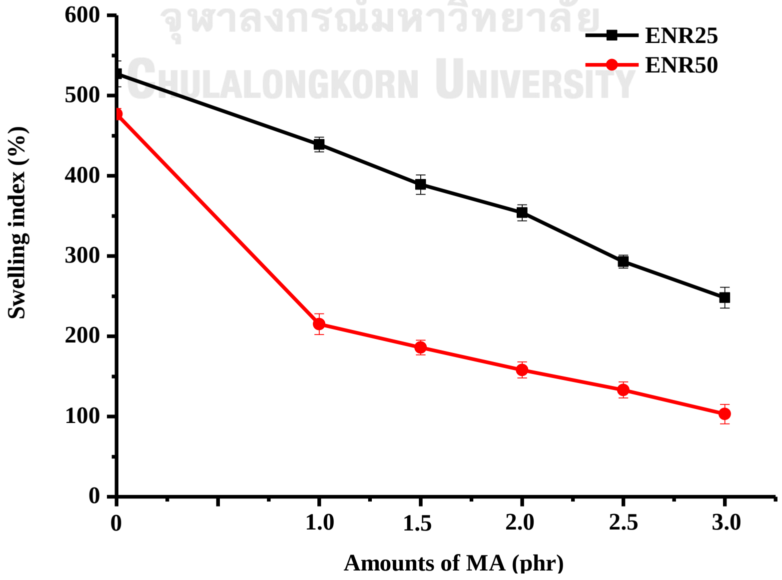


Figure 4.3 Swelling index (%) of ENR25 and ENR50 crosslinked with different amounts of MA

The result also showed the swelling index decreased with increasing in the amount of MA. This indicated that the degree of crosslinking was proportional to the amount of MA. It was observed at the same MA loading, ENR50 had much lower swelling index. This was because ENR50 was consisted of more oxirane rings which were active sites for crosslinking.

4.1.4 Cure Characteristics of ENR Crosslinked with MA

Cure characteristic of ENR25 and ENR50 crosslinked with various MA loadings at 150 ^{o}C were given in Figure 4.4 and Figure 4.5. Torque was plotted versus curing time. The increment of torque is attributed to the increase of crosslinking level. Generally, three cure characteristics including plateau, marching and reversion are observed in the over cure zone. The cure characteristic depends strongly on rubber type, curing system, and curing condition. The plateau behavior is indicated by a constant torque and is the desired outcome. The reversion occurs due to a breakage down of crosslink and degradation of rubber chains. The marching can be seen when the crosslinking reaction is continuously formed. Usually, ENR crosslinked with sulfur shows reversion behavior. In this study it was found that the ENR crosslinked with MA showed the marching behavior at the over cure zone as seen in Figure 4.5. The degree of crosslinking indicating by delta torque and crosslinking rate increased with the increase of MA loading. Moreover, it was noted that the crosslinking was taken very fast. The induction zone of curing was very short. As mentioned in the experimental, during compression molding at 150 ^{o}C, a smooth rubber sheet cannot be obtained from ENR50 cured with MA. This was because the crosslinking was taken place very fast. This did not allow the rubber to flow and fill in the mold cavity.

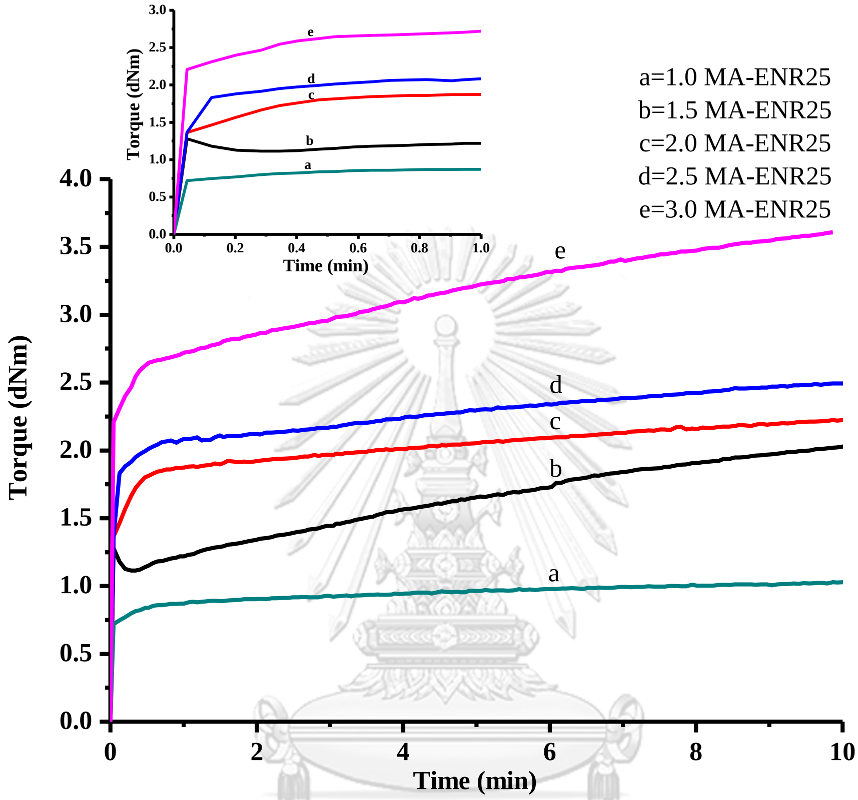


Figure 4.4 MDR rheographs of ENR25 crosslinked with different amounts of MA at 150 °C

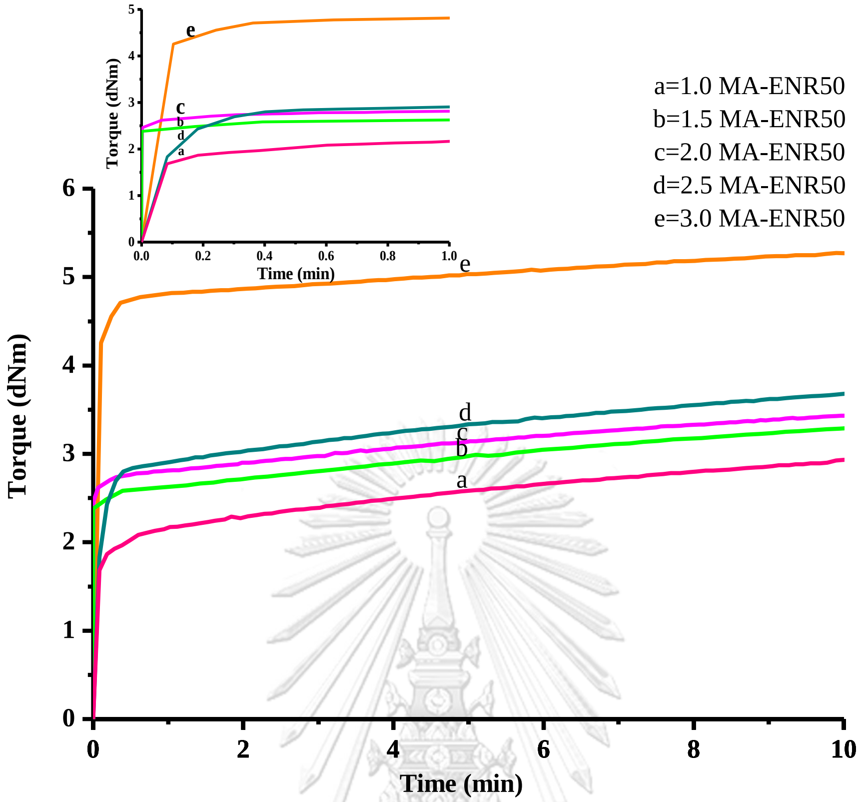


Figure 4.5 MDR rheographs of ENR50 crosslinked with different amounts of MA at 150 °C

4.1.5 Thermal Resistance of ENR Crosslinked with MA

The TGA thermograms of MA, uncrosslinked ENR25 and ENR25 crosslinked with 1 and 3 phr of MA are showed in Figure 4.6. From 50 °C to 1000 °C, all samples exhibited only one decomposition stage. MA decomposed at the lowest temperature around 200 °C. The decomposition of uncrosslinked ENR25 occurred around 400 °C. It was observed the ENR25 crosslinked with MA at 1.0 and 3.0 phr thermally decomposed at higher temperature than the uncrosslinked ENR25.

Thermal resistance of crosslinked ENR25 depended on crosslinking level. As seen, ENR25 crosslinked with 3 phr of MA decomposed at highest temperature.

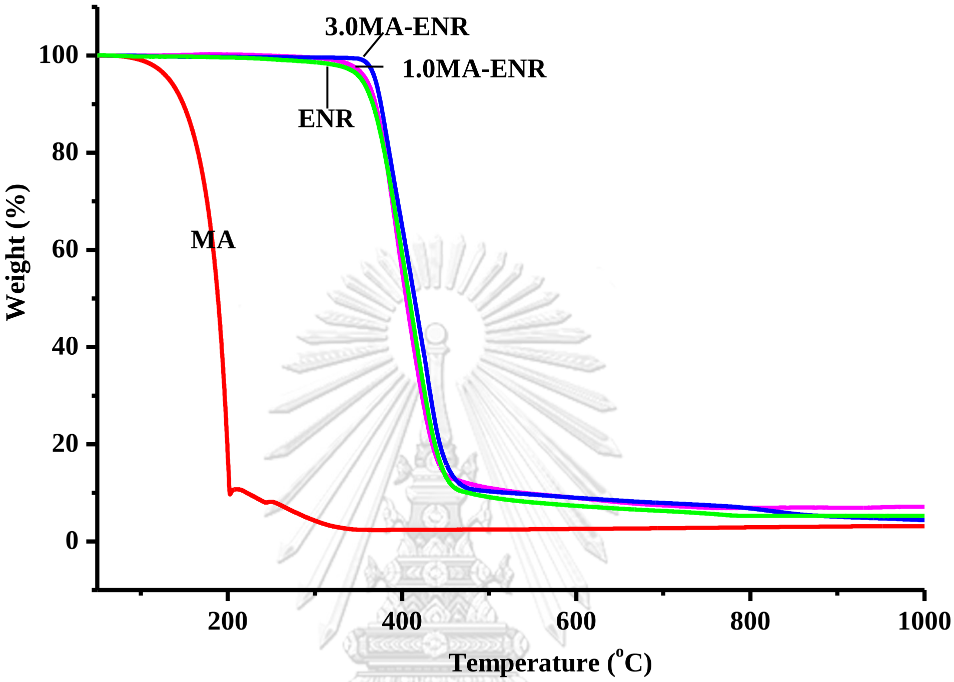


Figure 4.6 TGA thermograms of MA, uncrosslinked ENR25 and ENR25 crosslinked with 1.0 and 3.0 phr of MA

4.1.6 Tensile Properties of ENR Crosslinked with MA

Tensile properties of the uncrosslinked ENR25 and ENR25 crosslinked with different amounts of MA are tabulated in Table 4.3. Each property was depicted as a plot in Figure 4.7 to 4.10. It was noted that tensile properties of the ENR25 crosslinked with 1.0 phr of MA and none of ENR50 were not performed. This was because a smooth rubber sheet cannot be formed at all. Therefore, no tensile properties of these samples were available. Both 100% and 300% modulus representing the resistance to change the shape of sample upon tension force also increased with increasing MA content as seen Figures 4.7 and 4.8. The increment of modulus with increasing MA loading also indicated the sample had higher crosslink density. This result was agreed with the decrease in swelling index when increasing MA loading. From Figure 4.9, it can be clearly seen that the tensile strength of ENR25 can be increased when crosslinking with MA. The improvement of tensile strength increased with increasing MA content. Due to the restriction of chains, the elongation at break of all samples were decreased when the ENR25 was crosslinked as shown in Figure 4.10. The more crosslinking, the lower elongation at break.

Table 4.3 Tensile properties of uncrosslinked ENR25 and ENR25 crosslinked with different amounts of MA

Sample Name	**100% Modulus (MPa)**	**300% Modulus (MPa)**	**Tensile Strength (MPa)**	**Elongation at Break (%)**
Uncrosslinked ENR25	0.16 ± 0.04	0.18 ± 0.02	0.42 ± 0.11	1544 ± 121
1.0MA-ENR25	N/A	N/A	N/A	N/A
1.5MA-ENR25	0.80 ± 0.09	1.80 ± 0.12	3.44 ± 0.21	635 ± 43
2.0MA-ENR25	1.21 ± 0.14	1.98 ± 0.27	6.67 ± 0.48	554 ± 53
2.5MA-ENR25	1.22 ± 0.21	2.58 ± 0.39	6.95 ± 0.36	478 ± 32
3.0MA-ENR25	1.24 ± 0.28	2.71 ± 0.32	7.90 ± 0.57	456 ± 47

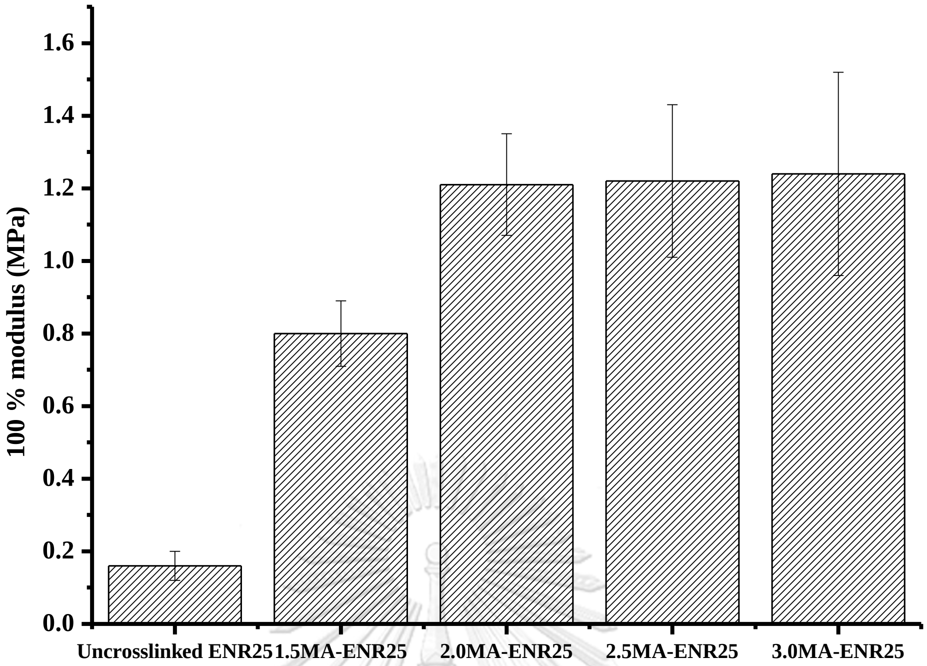


Figure 4.7 Comparison in 100% modulus between the uncrosslinked ENR25 and ENR25 crosslinked with different amounts of MA

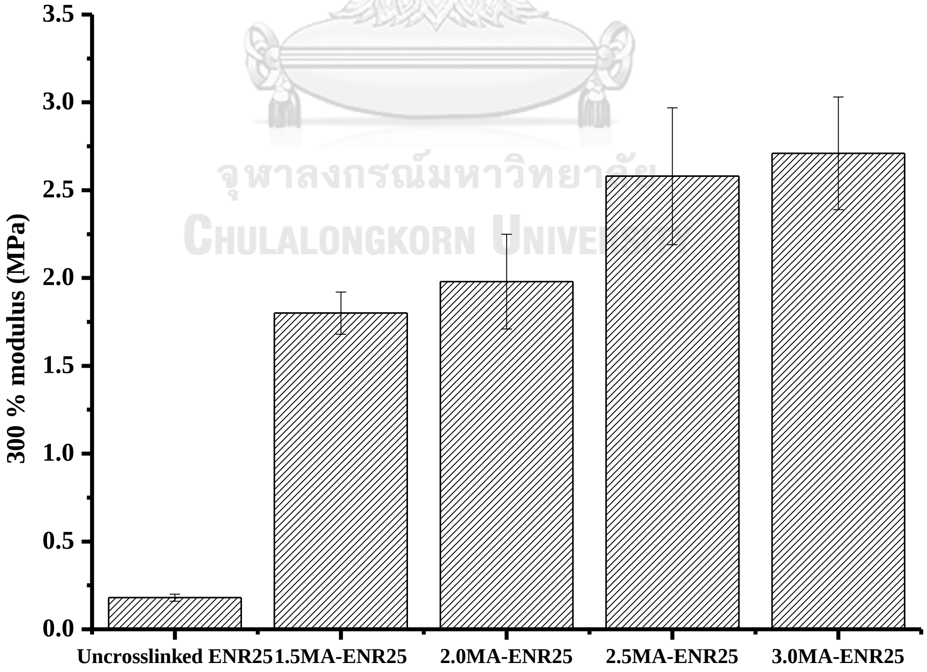


Figure 4.8 Comparison in 300% modulus between the uncrosslinked ENR25 and ENR25 crosslinked with different amounts of MA

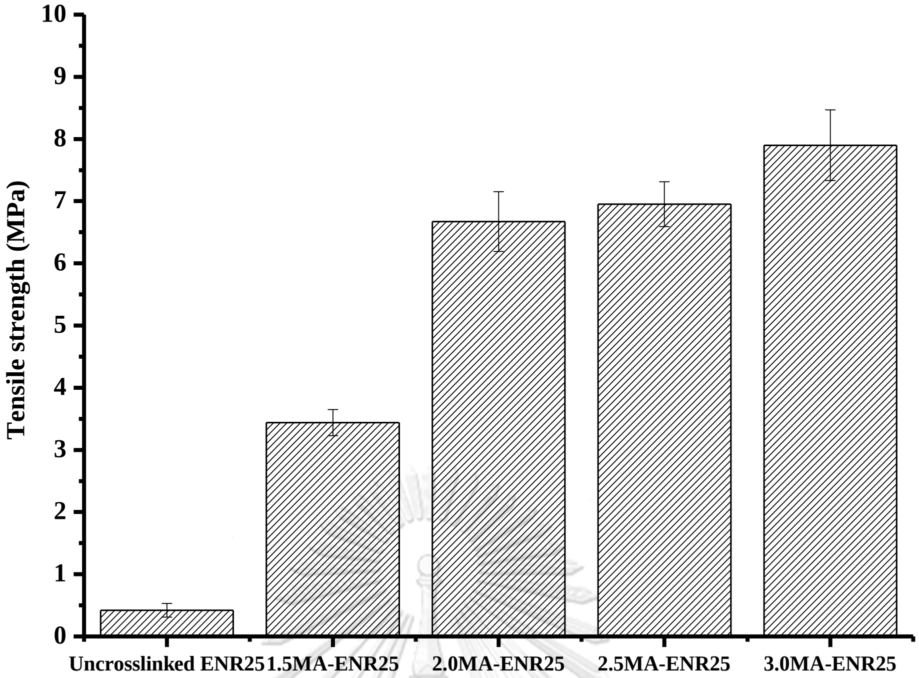


Figure 4.9 Comparison in tensile strength between the uncrosslinked ENR25 and ENR25 crosslinked with different amounts of MA

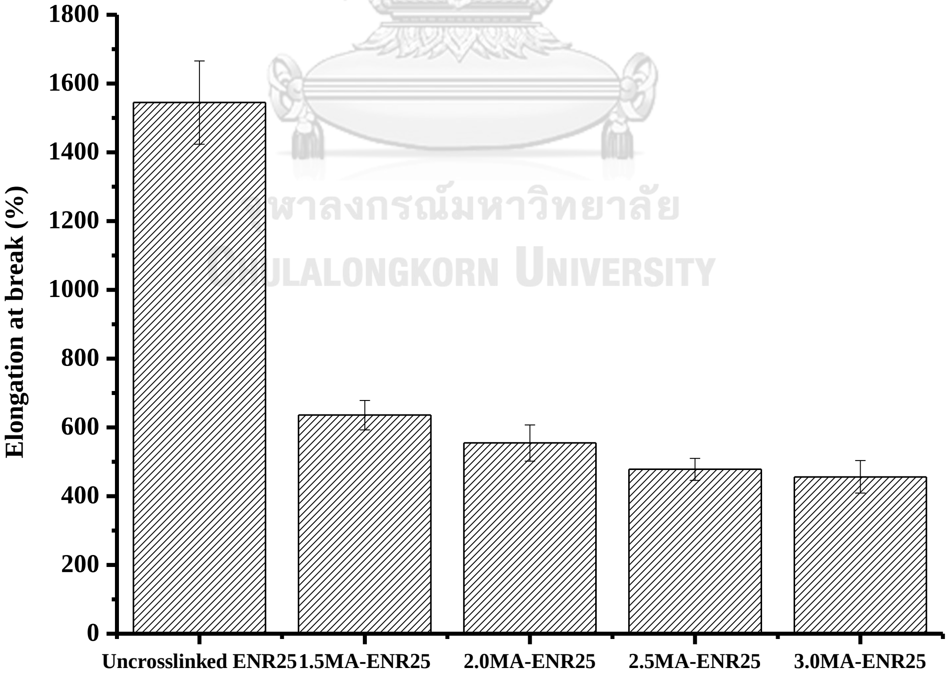


Figure 4.10 Comparison in % elongation at break between the uncrosslinked ENR25 and ENR25 crosslinked with different amounts of MA

4.2 Thermoreversible Crosslinking of Natural Rubber

4.2.1 Grafting Maleic Anhydride onto NR

To form thermoreversible crosslinking of natural rubber (NR), initially it is necessary to graft maleic anhydride (MA) onto the NR chains, thus giving a product called "maleated NR" or MNR. In this study, grafting reaction was carried out by reactive processing using an internal mixer without adding any peroxide catalyst. The effect of grafting condition and amount of MA on the degree of grafting were evaluated.

4.2.1.1 Chemical Structure of MNR

- *FT-IR spectra of MA, NR and MNR*

Figure 4.10 showed the FT-IR spectra of MA, pure NR and MNR. For the MA, peaks observed around 1835 (weaker) cm^{-1} and 1790 (stronger) cm^{-1} were contributed to the C=O in the succinic anhydride ring of MA[41]. For the pure NR, several peaks indicating the characteristics of isoprene unit were observed as followed; the peak around 835 cm^{-1} contributing to the =C-H wagging, the peak at 1375 cm^{-1} contributing to the C-H bending of CH_3 and the peak at 1440 cm^{-1} contributing to the C-H bending of CH_2 group[3]. In the case of the MNR, since the unreacted MA gives rise to absorption bands in the same regions as the grafted anhydride, the complete elimination of the unreacted MA is of great importance. This was done by washing with acetone during the precipitation process. The absence of unreacted MA can be verified by the disappearance of the characteristic band at 698 cm^{-1} (C=C bond of MA)[41]. In addition, it was clearly found that the FT-IR spectrum simply combined peaks from those of MA and NR. Moreover, the peak around 1710 cm^{-1} attributed to the carbonyl groups formed by the reaction of the anhydride functional groups with moisture[41]. The peak assignments are tabulated in Table 4.4.

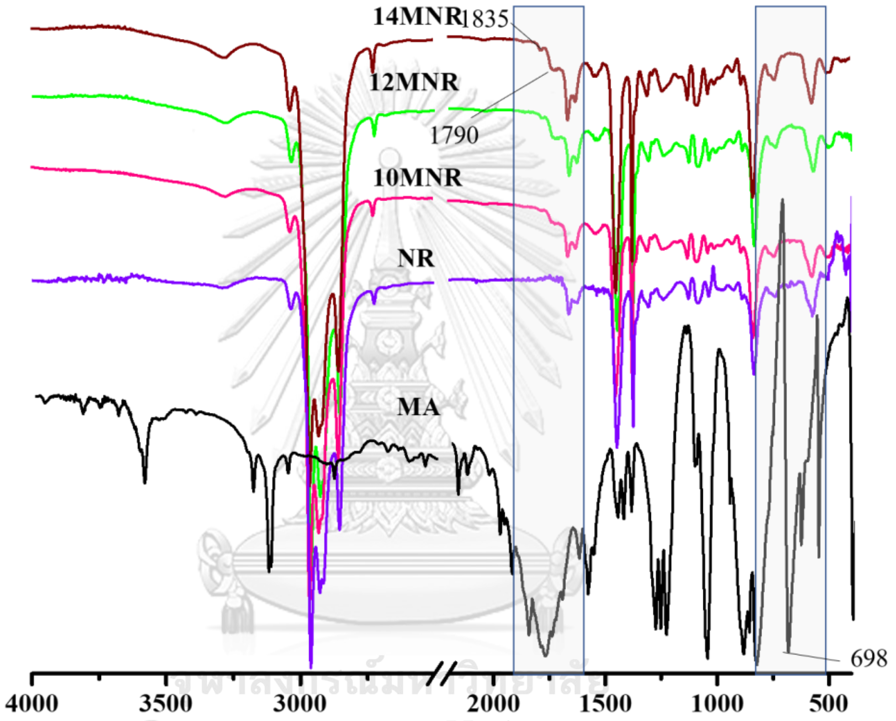


Figure 4.11 FT-IR spectra of MA, NR and MNR

- *^{1}H-NMR spectra of NR and MNR*

In Figure 4.11, the ^{1}H-NMR spectrum of the NR showed the characteristic signals of NR at 1.67, 2.03 and 5.12 ppm, which could be attributed to the methyl, methylene and unsaturated methane protons, respectively[32]. The MNR showed the same chemical shift as NR and the new chemical shift at 6.48 ppm indicated protons attached to a succinic anhydride group[45].

Table 4.4 FT-IR peak assignments of MA, NR and MNR.

Peak designation	Wave number (cm^{-1})
MA	
C=C, in anhydride	698
C=O, symmetric stretching (stronger) in anhydride	1790
C=O, asymmetric stretching (weaker) in anhydride	1835
NR	
C=C, bending	835
-CH-, deformations	1375
$-CH_2-$, deformations	1440
$-CH_2-$, symmetric stretching	2860
$-CH_2-$, asymmetric stretching	2926
$-CH_3-$, stretching	2960
$R_1R_2C=CHR_3$	3036
MNR	
C=O, stretching in carboxylic acid	1710
C=O, symmetric stretching (stronger) in anhydride	1790
C=O, asymmetric stretching (weaker) in anhydride	1835

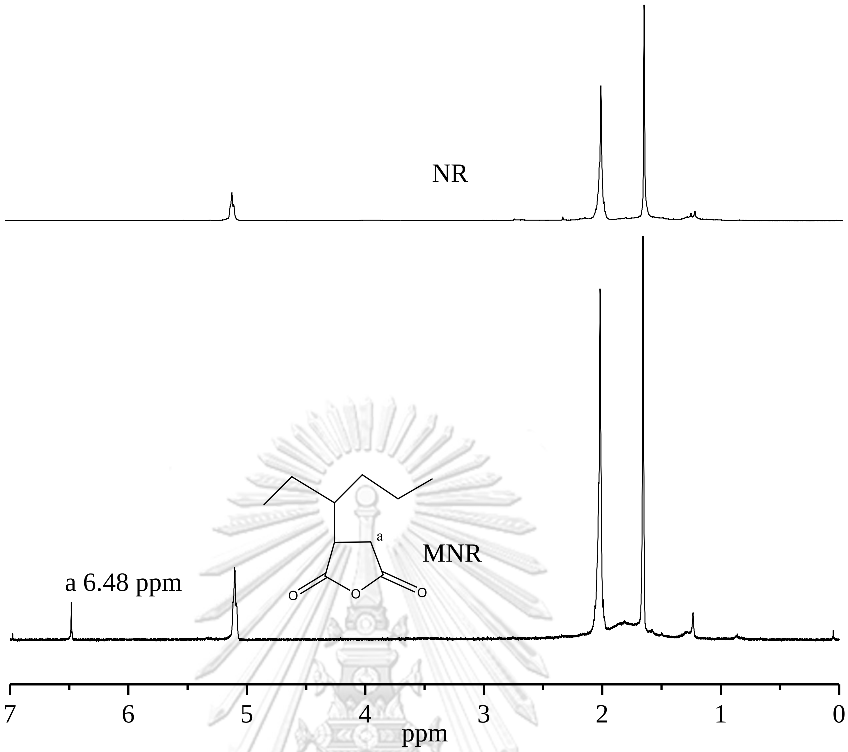


Figure 4.12 ^{1}H-NMR spectra of NR and MNR

4.2.1.2 The Proposed Grafting Reaction of MNR

From the above FT-IR and ^{1}H-NMR spectra, the proposed grafting reaction of MA onto the NR was schematically given in Figure 4.13. During mastication, the rubber chains were considered to be ruptured into free radicals via the sheer action. Then, these macroradicals abstracted allylic hydrogen atoms from the isoprene unit, forming macroradicals with free radicals along the main chain. When adding MA, these free radicals attacked the MA via the addition to double bond of MA, giving the MA grafted NR or MNR product.

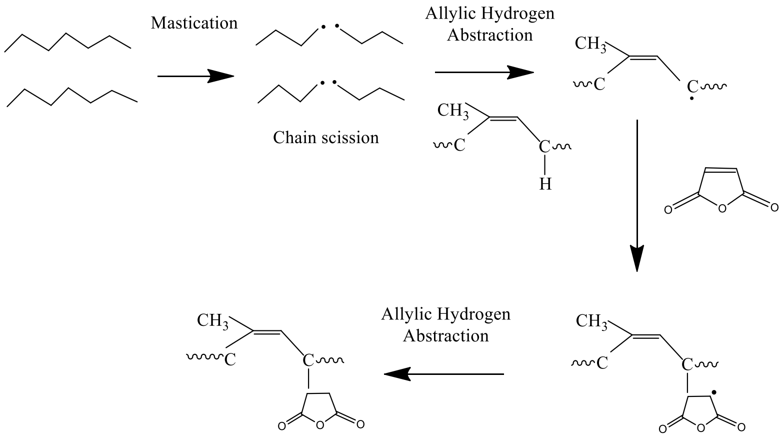


Figure 4.13 Proposed grafting reaction of MNR in the absence of initiator

4.2.1.3 % Grafting of MNR

The % grafting determined by a titration of acid groups derived from the anhydride functions with an alkaline solution from is given in Table 4.5. The grafting of MA onto the NR was successful by a reactive processing method in the absence of initiator. In the preliminary, the influence of mastication, reaction time and reaction temperature was studied. It can be clearly seen that % of grafting was dependent on the mastication, reaction time, reaction temperature and MA loading. In most cases, when increasing mastication and reaction time and reaction temperature, the % grafting passed through the maximum. However, the % grafting was directly proportional to the MA loading. The maximum % grafting obtained was 1.76 at optimum condition of 5 min of mastication time, 15 min of reaction time, 150 ^{o}C reaction temperature, and 14 phr of MA.

Table 4.5 % Grafting of MNR when varying processing condition and MA loadings.

Condition			% MA grafting		
Mastication time (min)	Reaction time (min)	Reaction Temperature (°C)	MA 10 phr	MA 12 phr	MA 14 phr
3	10	140	0.32±0.07	0.49±0.00	0.70±0.07
5	10	140	0.90±0.07	0.88±0.25	1.06±0.07
7	10	140	0.78±0.07	0.88±0.12	1.23±0.12
3	15	140	1.06±0.07	1.25±0.07	1.43±0.07
5	15	140	1.18±0.07	1.37±0.12	1.59±0.12
7	15	140	1.02±0.12	1.32±0.19	1.06±0.92
3	20	140	1.14±0.18	1.10±0.07	1.67±0.07
5	20	140	1.35±0.12	1.54±0.07	1.63±0.07
7	20	140	1.10±0.12	1.10±0.07	1.39±0.07
3	10	150	0.94±0.07	1.18±0.07	1.35±0.12
5	10	150	1.06±0.07	1.26±0.07	1.59±0.07
7	10	150	1.02±0.07	1.31±0.07	1.47±0.00
3	15	150	1.14±0.18	1.31±0.07	1.59±0.12
5	**15**	**150**	**1.31±0.14**	**1.43±0.07**	**1.76±0.07**
7	15	150	1.06±0.07	1.35±0.12	1.59±0.00
3	20	150	1.02±0.07	1.43±0.07	1.47±0.00
5	20	150	0.98±0.12	1.43±0.07	1.38±0.07
7	20	150	0.90±0.18	1.31±0.07	1.47±0.21
3	10	160	0.45±0.25	0.70±0.07	0.86±0.00
5	10	160	0.57±0.07	1.02±0.07	1.10±0.12
7	10	160	0.78±0.35	1.14±0.07	1.39±0.07
3	15	160	0.45±0.25	0.69±0.07	0.86±0.00
5	15	160	0.58±0.07	1.02±0.07	1.10±0.12
7	15	160	0.78±0.35	1.14±0.07	1.39±0.07
3	20	160	0.82±0.07	1.31±0.07	1.39±0.07
5	20	160	0.90±0.14	1.18±0.07	1.27±0.18
7	20	160	0.65±0.07	0.93±0.07	1.14±0.07

When increasing mastication time and reaction time, it was found that the degree of grafting passed through the maximum. Initially, the increase in mastication led to the higher amount of free radical, thus giving higher % grafting. The further increase in the mastication time (from 5 to 7 min) led to the reduction of the % grafting. When the higher amounts of free radicals were formed. It was highly possible for these free radicals to recombine, thus leading to the decreased % grafting. Same reaction was applied when increasing reaction time. Moreover, in the study the amount of MA was increased from 10 to 12, 14 and 16 phr. However, it was found that at the 16 phr, the % grafting was about 1.72 % which was almost similar to the one obtained at 14 phr. So that, in this study the optimum grafting was at 14 phr of MA, 5 min of mastication time, 15 min of reaction time, 150 °C reaction temperature.

4.3 Formation of Thermoreversible Crosslinking MNR with Glycerol

4.3.1 FT-IR spectra Before and After thermoreversible Crosslinking MNR with Glycerol

The formation of thermoreversible crosslinking was confirmed by FT-IR result (Figure 4.14 and Table 4.6). Initially, as mentioned in the previous section, the main characteristic peaks of MNR were found at 1835 cm^{-1} (weaker) and 1790 cm^{-1} (stronger) due to C=O group in the succinic anhydride ring. After mixing MNR with glycerol without heating, the FT-IR spectrum showed a broad peak at 3400 cm^{-1}, representing the OH stretching mode of glycerol. The two characteristics peaks of the succinic anhydride ring were also observed. This confirmed that the thermoreversible crosslinking was not taken place. Once the mixture was heated up to 150 °C for 10 min and then cooled down to 25 °C, one newly formed peak was observed at 1735 cm^{-1}. The emergence of an ester peak indicated the occurrence of C=O stretching vibration of the ester. Furthermore, a peak at 1710 cm^{-1} indicated C=O stretching vibration of carboxyl groups. The formation of these two peaks indicated the occurrence of the reaction between MNR and glycerol via the ring opening of MA.

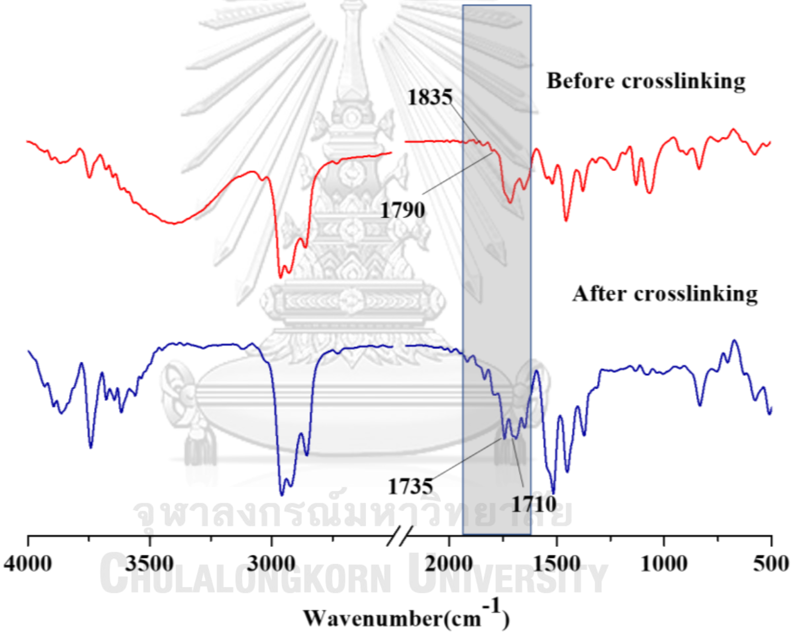


Figure 4.14 FT-IR spectra before and after thermoreversible crosslinking MNR with glycerol

4.3.2 The Proposed Thermoreversible Crosslinking of MNR with Glycerol

The thermoreversible crosslinking of MNR with glycerol can be occurred by the ring opening on the succinic anhydride ring of the MNR. Figure 4.15

showed the proposed thermoreversible crosslinking reaction of the crosslinking MNR with glycerol. The hydroxyl group of glycerol reacted with the carboxylic groups along the rubber chains, thus causing a ring opening of succinic ring and producing the ester linkages between the rubber chains.

Table 4.6 FT-IR peak assignments before and after thermoreversible crosslinking MNR with glycol

Peak designation	Wave number (cm^{-1})
Before thermoreversible crosslinking MNR with glycerol	
C=C, bending	835
-CH-, deformations	1375
-CH$_2$-, deformations	1440
C=O, symmetric stretching (stronger) in anhydride	1790
C=O, asymmetric stretching (weaker) in anhydride	1835
-CH$_2$-, symmetric stretching	2860
-CH$_2$-, asymmetric stretching	2926
-CH$_3$-, stretching	2960
R$_1$R$_2$C=CHR$_3$	3036
-OH, stretching	3400
After thermoreversible crosslinking MNR with glycerol	
C=O, stretching in carboxylic acid	1710
C=O, stretching in ester	1735

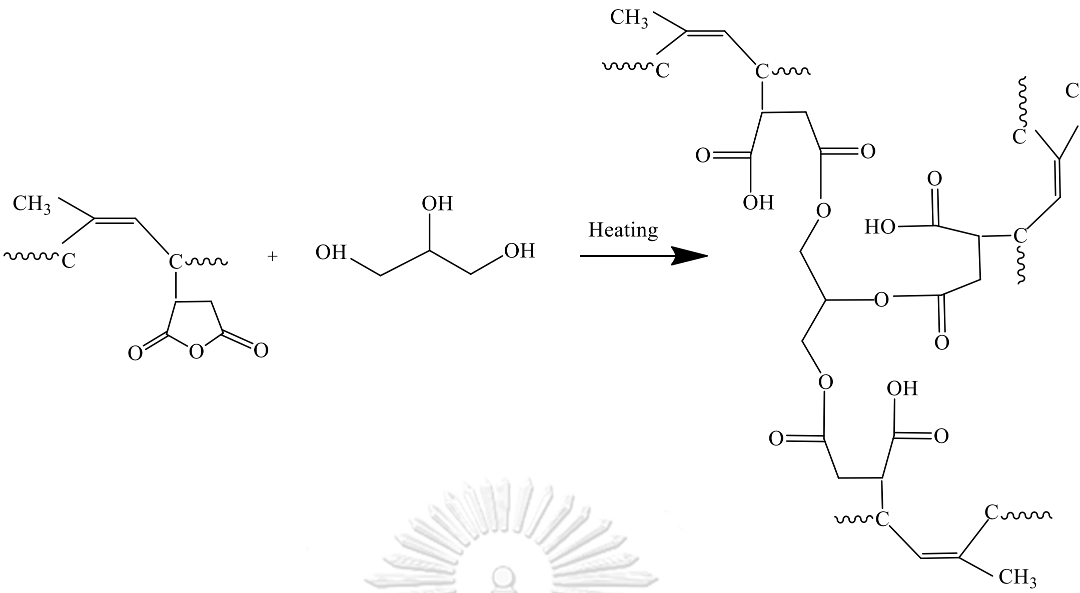


Figure 4.15 The proposed thermoreversible crosslinking reaction of the MNR with glycerol

4.3.3 Swelling Index (%) of Thermoreversible Crosslinking MNR with Glycerol

In order to confirm the formation of thermoreversible crosslinking between the MNR chains with glycerol, the swelling index (%) of the heated MNR/glycerol mixture at various glycerol loadings of 5, 10, 15 and 20 phr was determined and shown in Figure 4.16. In case of pure MNR, it was found that the sample was not completely dissolved. This might be because the moisture was able to open the succinic ring of MA, leading to the thermoreversible crosslinking of MNR[41]. In the case of the heated MNR/glycerol samples, it was seen that degree of swelling was considerably lower as compared to the pure MNR. This fact confirmed that the MNR was successfully crosslinked with glycerol. Again, the value of swelling level of heated MNR/glycerol samples was strongly dependent on the glycerol content. As shown in Figure 4.16, the lowest value of swelling level was found in 14MNR-20Gly sample. This was the evidence of highest degree of crosslinking for 14MNR-20Gly among the different MNR samples crosslinked with glycerol.

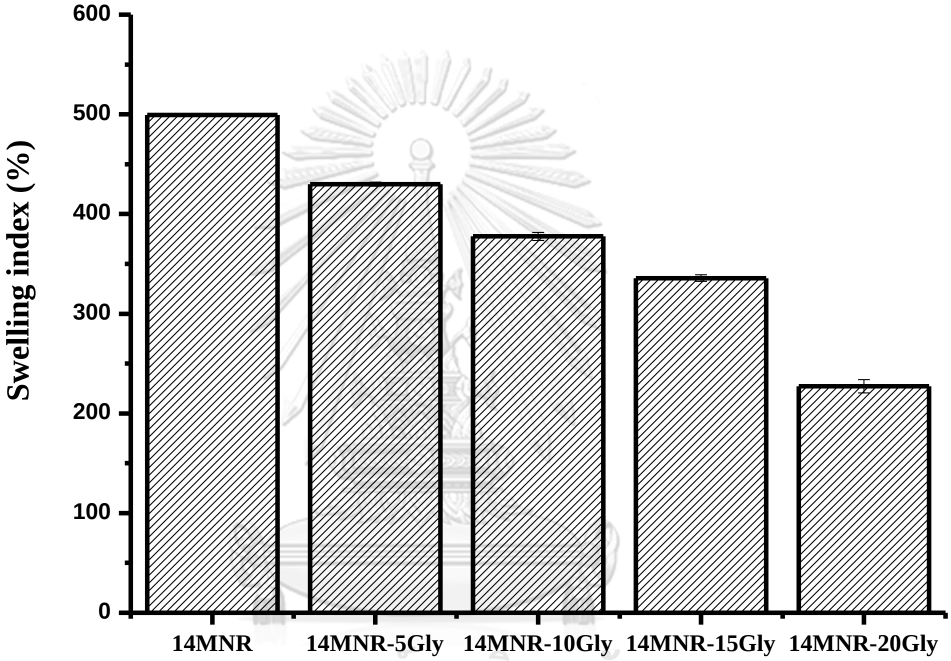


Figure 4.16 Swelling index (%) of thermoreversible crosslinking MNR with different amounts of glycerol

4.3.4 Tensile Properties of Thermoreversible Crosslinking MNR with Glycerol

Tensile properties of thermoreversible crosslinking MNR with glycerol at various contents were compared with those of the uncrosslinked MNR as tabulated in Table 4.7. Each property was depicted as a plot in Figure 4.17 to 4.20. Both 100% and 300% modulus representing the resistance to change the shape of sample upon tension force also increased with increasing glycerol contents. It was clearly observed that the tensile strength of crosslinked MNR compounds increased steadily with increasing glycerol contents. This was due to the increase of covalent crosslinking formed between the rubber chains with increasing glycerol contents. Due to the restriction of chains, the elongation at break of all samples were decreased when the MNR was crosslinked. Obviously, the value of elongation at break decreased constantly with increasing amount of crosslinking.

Table 4.7 Tensile properties of thermoreversible crosslinking 14MNR with different amounts of glycerol

Sample Name	100% Modulus (MPa)	300% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
14MNR	0.16±0.02	0.17±0.01	0.18±0.09	1313±14
14MNR-5Gly	0.36±0.04	0.38±0.04	0.42±0.29	1245±33
14MNR-10Gly	1.38±0.05	1.56±0.07	1.68±0.13	1076±22
14MNR-15Gly	2.29±0.05	2.38±0.04	4.13±0.47	966±12
14MNR-20Gly	3.66±0.11	3.78±0.06	7.24±0.38	837±7

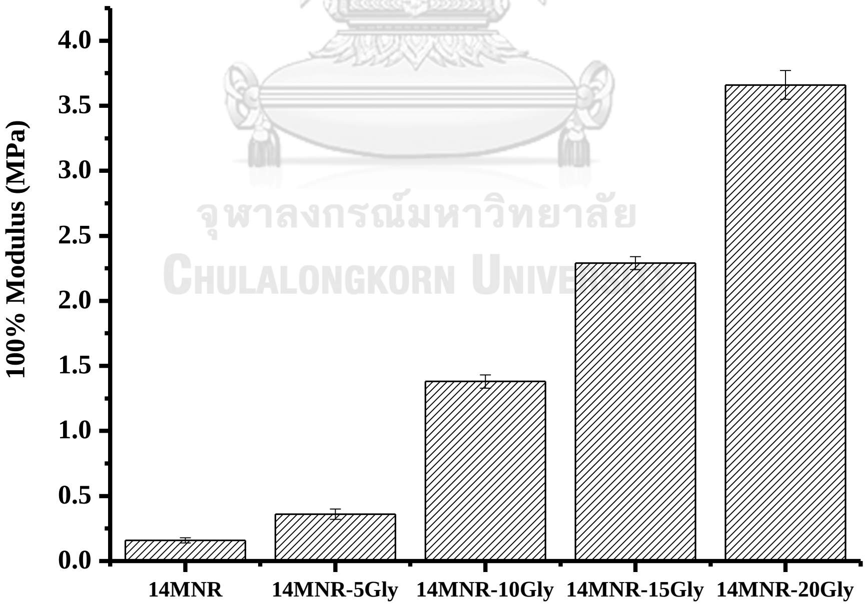


Figure 4.17 100% Modulus of thermoreversible crosslinking 14 MNR with different amounts of glycerol

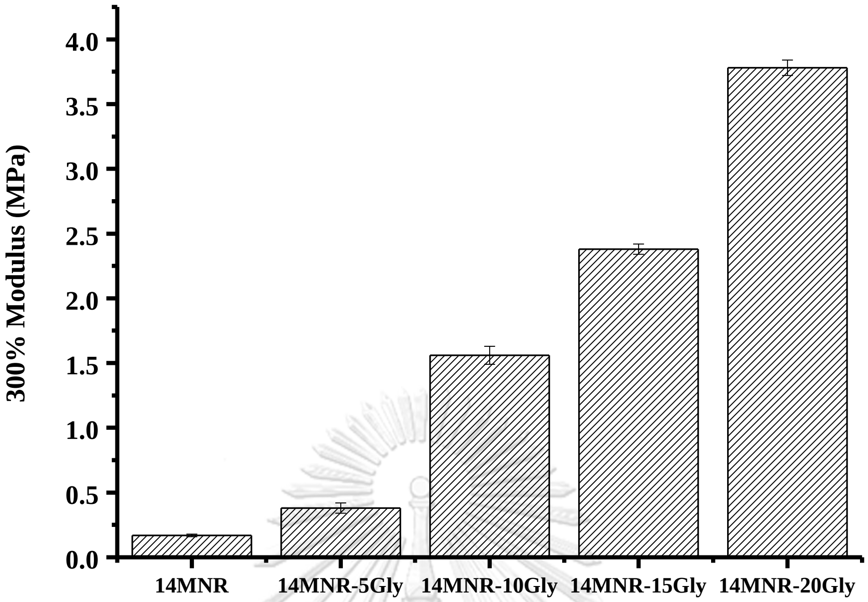


Figure 4.18 300% Modulus of thermoreversible crosslinking 14MNR with different amounts of glycerol

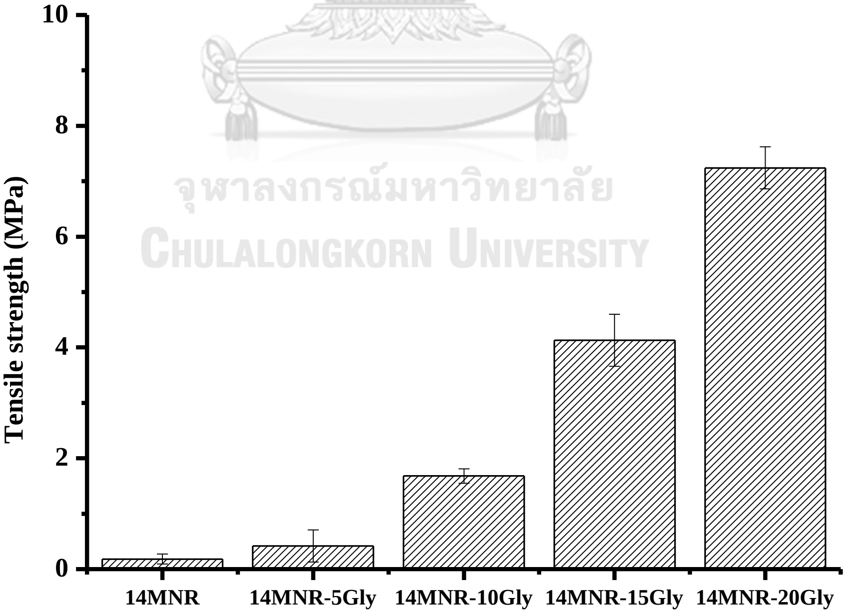


Figure 4.19 Tensile strength of thermoreversible crosslinking 14MNR with different amounts of glycerol

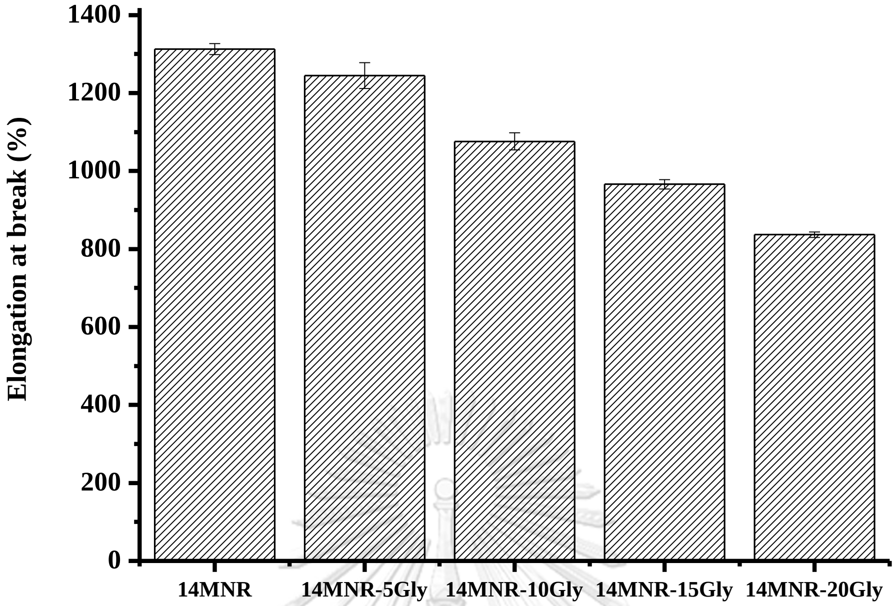


Figure 4.20 Elongation at break (%) of thermoreversible crosslinking 14MNR with different amounts of glycerol

4.3.5 Reprocessability of Thermoreversible Crosslinking MNR with Glycerol

To confirm the reprocessability of the MNR crosslinked with glycerol, the crosslinked samples were cut into a small piece and remolded again above the temperature showing an exothermal step-change (~ ≥ 150 °C observed from Figure 4.21). In this work, the reprocessability was carried out at 150 °C. It was observed that during remolding at this temperature, the sample could be reshaped again. This indicated that the MNR crosslinking with glycerol could be reprocessed at 150 °C. Reprocessability of the MNR crosslinked with glycerol was also carried out with other methods as followed.

- DSC thermogram of Thermoreversible Crosslinking MNR with Glycerol

The formation of glycerol crosslinked MNR was investigated from DSC thermogram as shown in Figure 4.21. When the MNR/glycerol mixture was heated from 40 to 170 °C, the obtained heating curve showed the exothermal step-change at 110-140 °C. This was attributed to the formation of crosslinking between maleic anhydride and hydroxyl groups of glycerol, giving the ester covalent crosslinking network. On the other hand, the cooling curve was not observed any step-change. However, after being treated by one to three heating-cooling cycles, DSC curves still showed exothermal step-changes at around the same position. This indicated that those broken ester covalent bonds can be reformed again. Thus, it is possible to reprocess/or remold the MNR crosslinked with glycerol. In the addition, in the case of pure MNR the exothermal reaction peak was not observed.

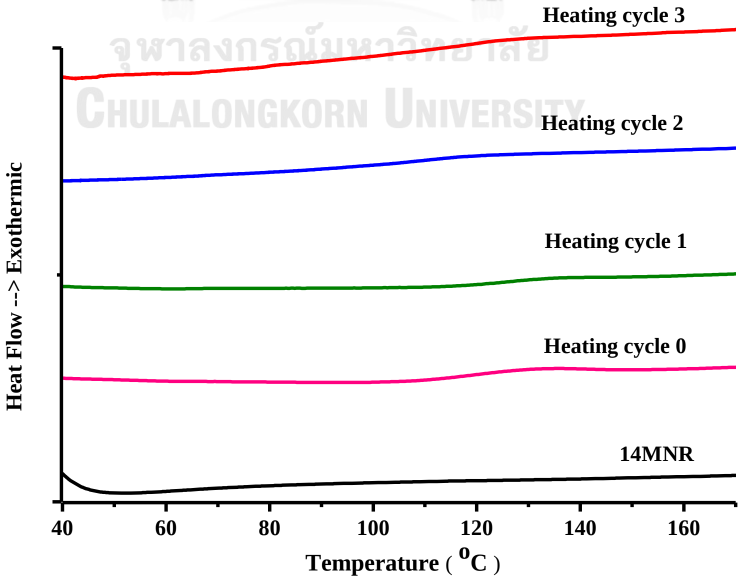


Figure 4.21 DSC curves of 14MNR-20Gly at the increment heating cycle

- FT-IR spectra of Thermoreversible Crosslinking MNR with Glycerol at the Increment Heating Cycle

Figure 4.22 showed the change of realtime FT-IR spectra of thermoreversible crosslinking 14MNR with 20 phr of glycerol when heating/cooling at 150/25 °C for 3 recycling times. Initially, as seen the glycerol crosslinked MNR showed the characteristic bands of ester and carboxylic acid bands around 1735 cm^{-1} and 1710 cm^{-1}, respectively. To analyze the equilibrium reaction thermodynamics[21, 23], the thermoreversible crosslinked sample was heated to 150 °C, leading to the decreased intensity of the carboxylic acid band (1710 cm^{-1}) but the increased intensity of anhydride band (1790 cm^{-1}). The most evident explanation for these changes was that a significant fraction of hemi-ester was converted to anhydride groups according to Figure 4.15. This reaction, which was actually a simple acid/alcohol esterification, did not occur at low temperatures, but may become more prominent at elevated temperatures[21, 23]. However, during cooling down to 25 °C, the formation of crosslink was recovered. This was indicated by the increased intensity of carboxylic acid band. The same behavior was also observed during the second and third heating/cooling cycle.

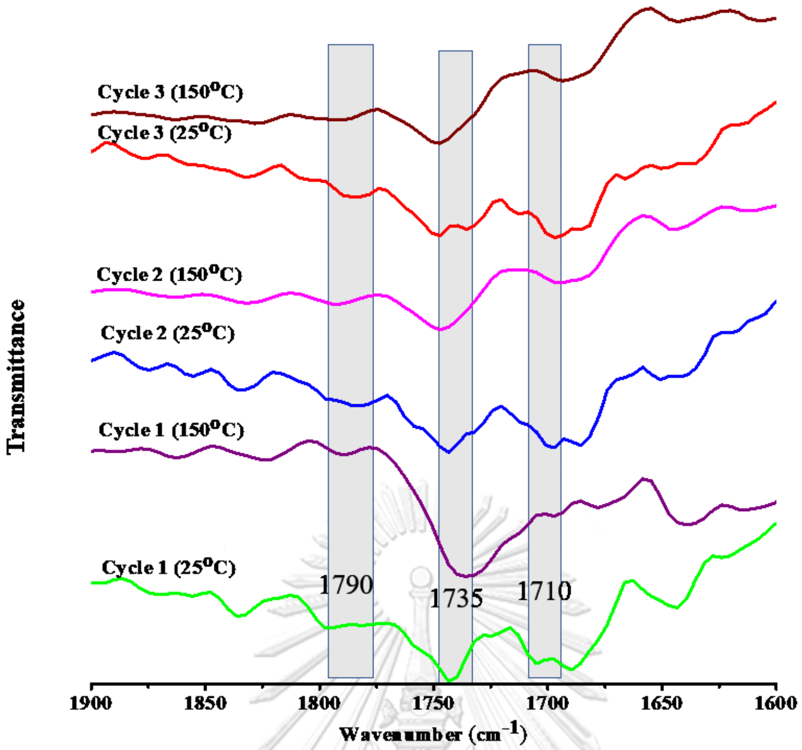


Figure 4.22 Realtime FT-IR spectrum of 14MNR-20Gly when heating to 150 °C at the increment heating-cooling cycle

- Tensile Properties of Thermorevrsible Crosslinking MNR with Glycerol at the Increment Heating Cycle

Tensile properties of the reprocessed MNR crosslinked with glycerol at increment recycling rounds were shown in Table 4.8. Each property was depicted as a plot in Figure 4.23 to 4.26. The sample with one recycle round had highest tensile strength and modulus but slightly lower than those of the pristine sample. The tensile strength was found to decrease when the round of recycling increased. However, the tensile strength of sample remolded three times was still higher than the uncrosslinked MNR. Possibly, the deterioration of strength was not only due to the reduction of crosslinking density indicating by the lower modulus at increment recycling rounds but also the thermal degradation of rubber itself during remolding.

Table 4.8 Tensile properties of 14MNR-20Gly at increment recycling round.

Sample Name	100% Modulus (MPa)	300% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
14MNR-20Gly	3.53±0.09	3.65±0.08	7.09±0.11	982±4
Heating cycle1	2.47±0.08	2.68±0.13	6.37±0.18	769±13
Heating cycle2	1.37±0.02	1.62±0.09	3.89±0.05	682±14
Heating cycle3	0.86±0.07	0.93±0.04	2.17±0.15	538±7
14MNR	0.16±0.02	0.17±0.01	0.18±0.09	1313±14

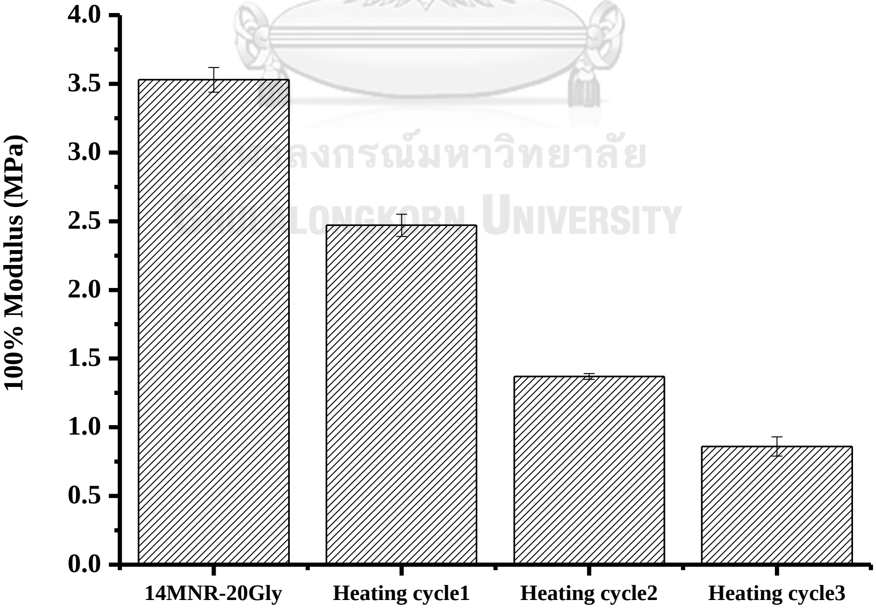


Figure 4.23 100% Modulus of 14MNR-20Gly at increment recycling round

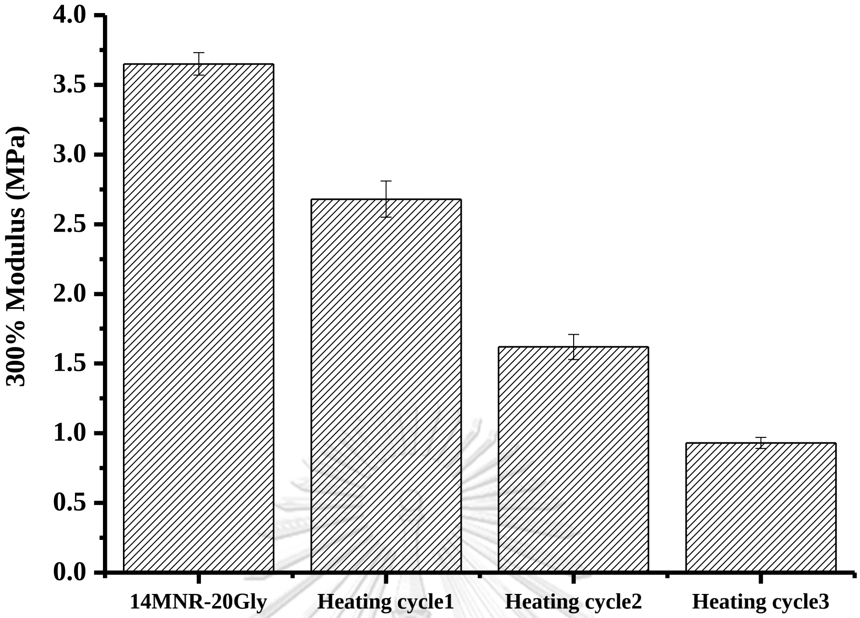


Figure 4.24 300% Modulus of 14MNR-20Gly at increment recycling round

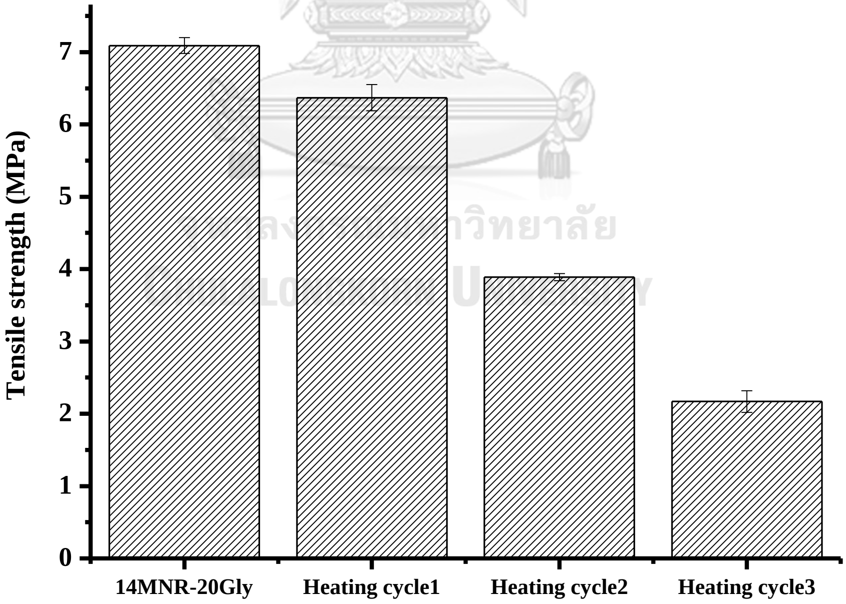


Figure 4.25 Tensile strength of 14MNR-20Gly at increment recycling round

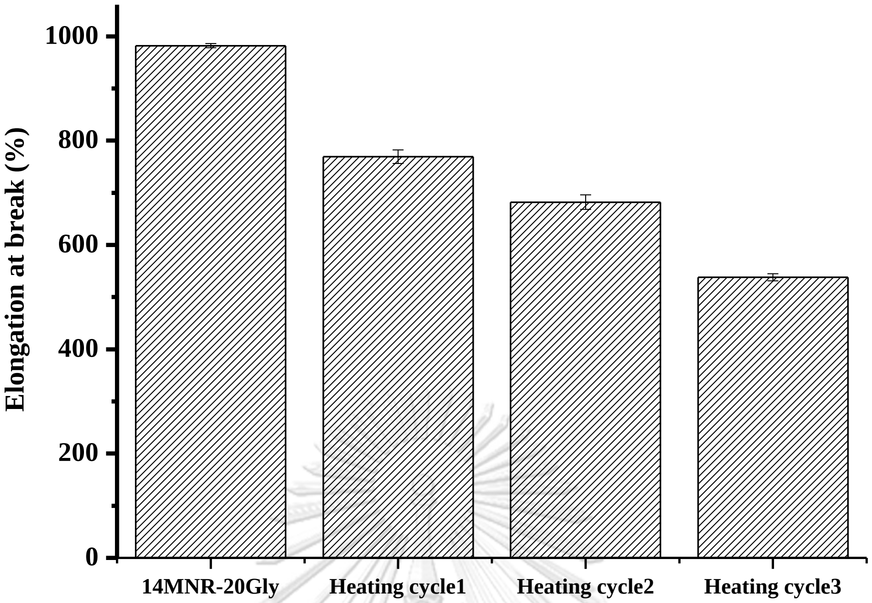


Figure 4.26 Elongation at break (%) of 14MNR-20Gly at increment recycling round

4.4 Formation of Thermoreversible Crosslinking MNR with Diethylene Glycol

4.4.1 FT-IR spectra of Before and After Thermoreversible Crosslinking MNR with Diethylene Glycol

FT-IR spectra of before and after thermoreversible crosslinking MNR with diethylene glycol were given in Figure 4.27. For MNR premixing with diethylene glycol but not crosslinking yet, the spectrum was consisted of the main characteristic peak of MNR at 1835 (weaker) cm^{-1} and 1790 (stronger) cm^{-1} to the referring to C=O in the succinic anhydride ring of MA and also a broad peak at 3400 cm^{-1}, representing the OH stretching mode of diethylene glycol. Similar to the MNR thermoreversible crosslinking with glycerol, after heating MNR mixed with diethylene glycol to 150 °C for 10 min and then cooled down to 25 °C, the occurrence of C=O stretching vibration of the ester and C=O stretching vibration of carboxyl groups were found. Moreover, it was clearly observed that the peak of OH group of diethylene glycol significantly decreased. This indicated the MNR was crosslinked with diethylene glycol via the ring opening of MA grafted on the MNR chains. The peak assignments were listed in Table 4.9.

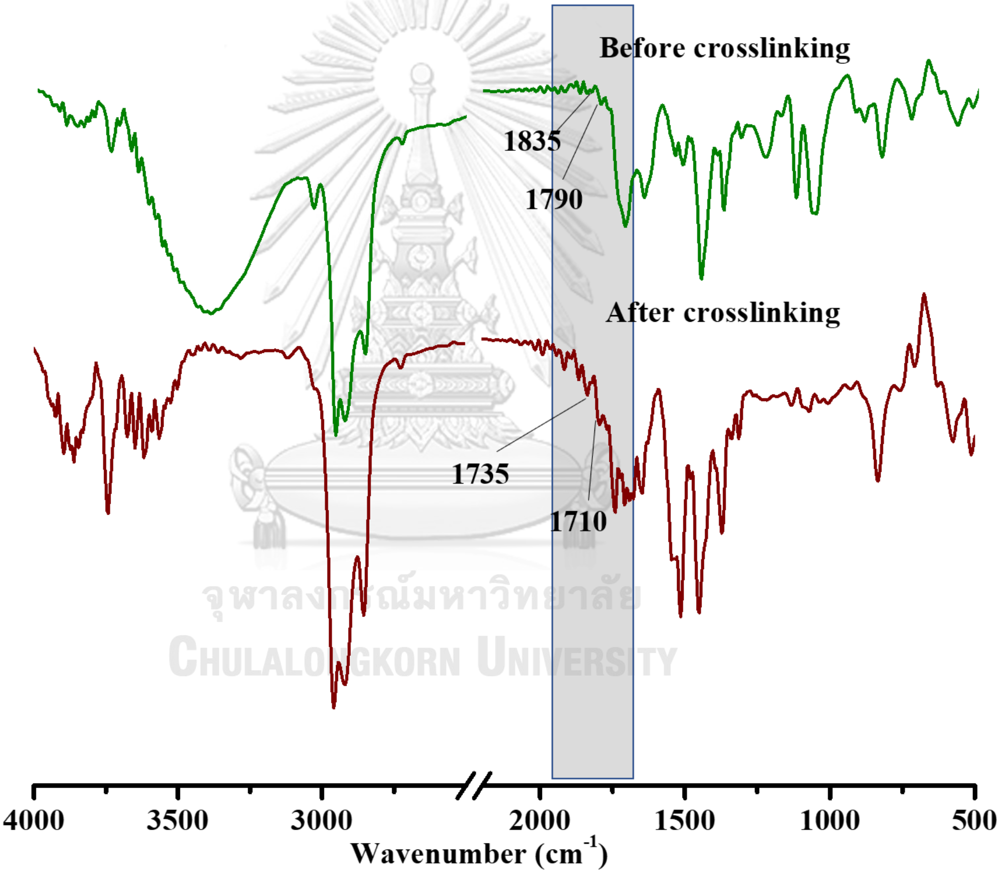


Figure 4.27 FT-IR spectra of before and after thermoreversible crosslinking MNR with diethylene glycol

Table 4.9 FT-IR peak assignments of before and after thermoreversible crosslinking MNR with diethylene glycol

Peak designation	Wave number (cm^{-1})
Before thermoreversible crosslinking MNR with diethylene glycol	
C=C, bending	835
C-O-C, asymmetric stretching	870
C-O-C, symmetric stretching	1247
-CH-, deformations	1375
$-CH_2-$, deformations	1440
C=O, symmetric stretching (stronger) in anhydride	1790
C=O, asymmetric stretching (weaker) in anhydride	1835
$-CH_2-$, symmetric stretching	2860
$-CH_2-$, asymmetric stretching	2926
$-CH_3-$, stretching	2960
$R_1R_2C=CHR_3$	3036
OH, stretching	3400
After thermoreversible crosslinking MNR with diethylene glycol	
C=O, stretching in carboxylic acid	1710
C=O, stretching in ester	1735

4.4.2 The Proposed Thermoreversible Crosslinking of MNR with Diethylene Glycol

Figure 4.28 showed the proposed thermoreversible crosslinking reaction of the crosslinking MNR with diethylene glycol. The crosslinking was taken place via a ring opening reaction of succinic ring with the hydroxyl group of diethylene glycol, producing the ester linkages between the rubber chains. Although diethylene glycol and glycerol crosslinked MNR with the similar mechanism. However, the MNR crosslinked with diethylene glycol can only form a di-functional crosslinking structure, whereas the MNR crosslinked with glycerol can form a tri-functional crosslinking structure.

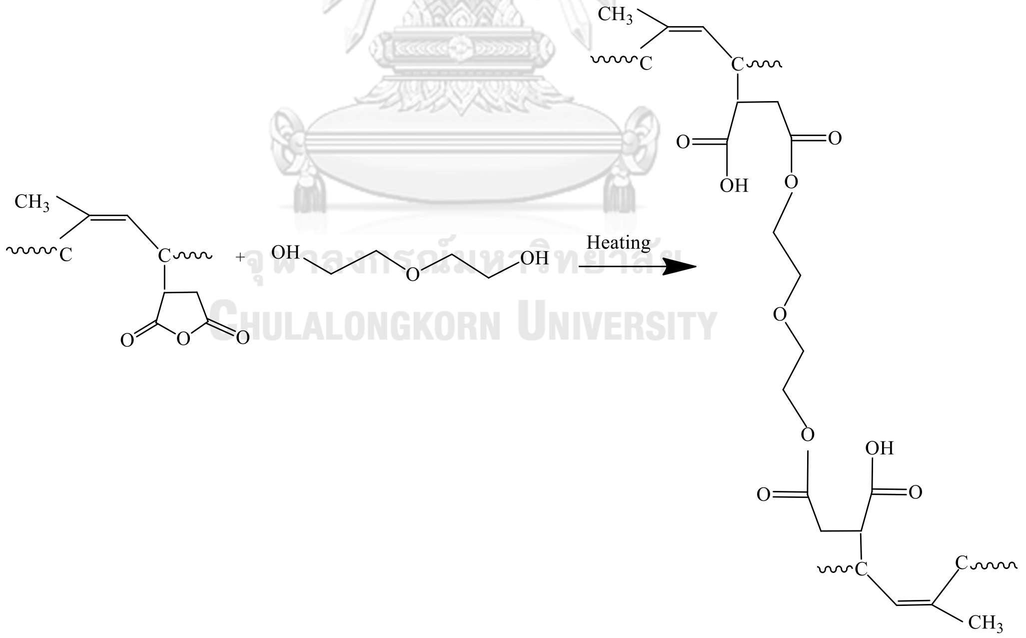


Figure 4.28 The proposed thermoreversible crosslinking reaction of the MNR with diethylene glycol

4.4.3 Swelling Index (%) of Thermoreversible Crosslinking MNR with Diethylene Glycol

The swelling index (%) of the heated MNR/DGly mixture at various diethylene glycol (DGly) loadings of 5, 10, 15 and 20 phr was shown in Figure 4.29. It was found that % of swelling of the heated MNR/DGly samples was lower than that of the pure MNR. This result confirmed that the MNR was successfully crosslinked with diethylene glycol. Moreover, it was found that the value of % swelling of heated MNR/DGly samples was strongly dependent on the diethylene glycol content. The MNR/DGly samples with higher diethylene glycol content gave lower % swelling.

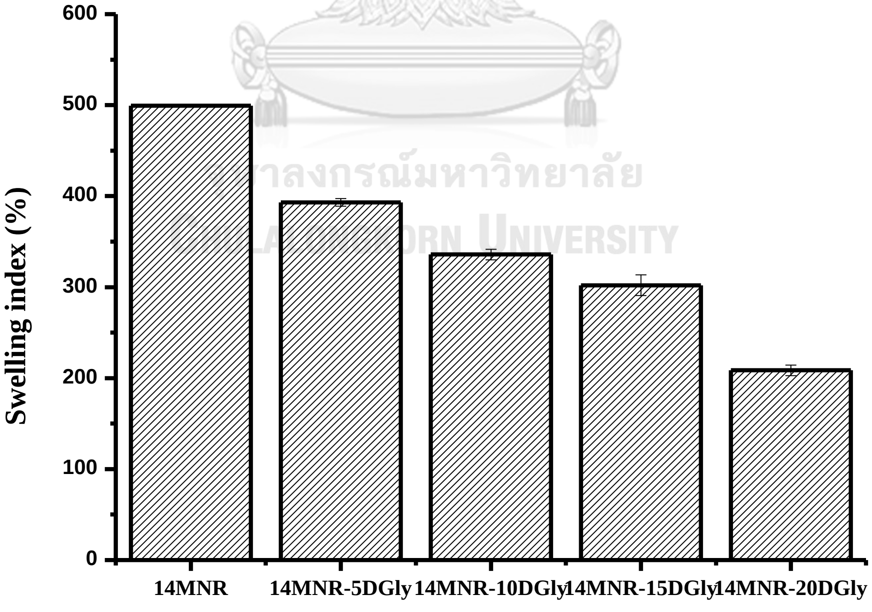


Figure 4.29 Swelling index (%) of thermoreversible crosslinking MNR with different amounts of diethylene glycol

4.4.4 Tensile Properties of Thermoreversible Crosslinking MNR with Diethylene Glycol

Table 4.10 showed tensile properties of MNR crosslinked with different amounts of diethylene glycol and the uncrosslinked MNR. Each property was depicted as a plot in Figure 4.30 to 4.33. The result showed that the 100% modulus, 300% modulus which are directly proportional to the crosslinking level increased with increasing diethylene glycol contents. Therefore, the increasing in tensile strength with increasing diethylene glycol contents was due to the increased crosslinking level. This also led to the decrease in the elongation at break of samples when increasing with increasing diethylene glycol contents.

Table 4.10 Tensile properties of thermoreversible crosslinking 14MNR with different amounts of diethylene glycol.

Sample Name	100% Modulus (MPa)	300% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
14MNR	0.16±0.02	0.17±0.01	0.18±0.09	1313±14
14MNR-5DGly	0.50±0.06	0.77±0.07	0.74±0.03	1143±7
14MNR-10DGly	1.83±0.08	1.91±0.03	1.94±0.05	982±7
14MNR-15DGly	2.58±0.04	2.70±0.06	5.65±0.11	880±11
14MNR-20DGly	3.96±0.04	4.37±0.05	9.12±0.17	782±7

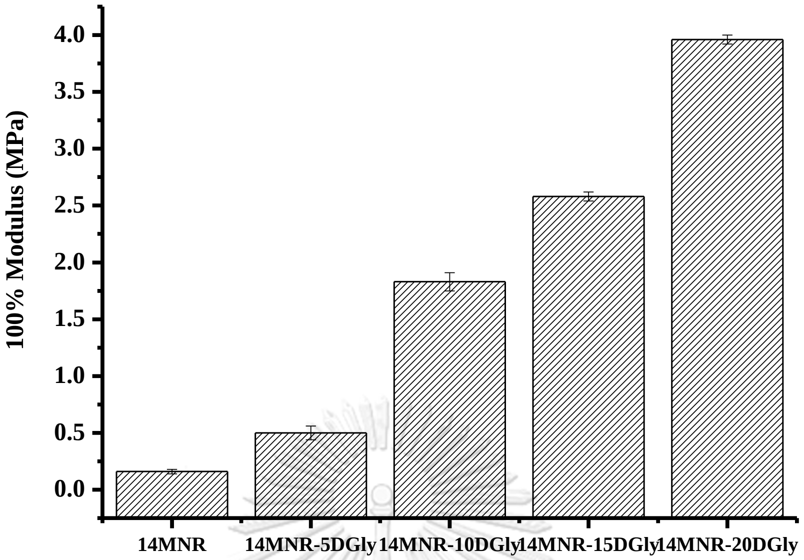


Figure 4.30 100% Modulus of thermoreversible crosslinking 14MNR with different amounts of diethylene glycol

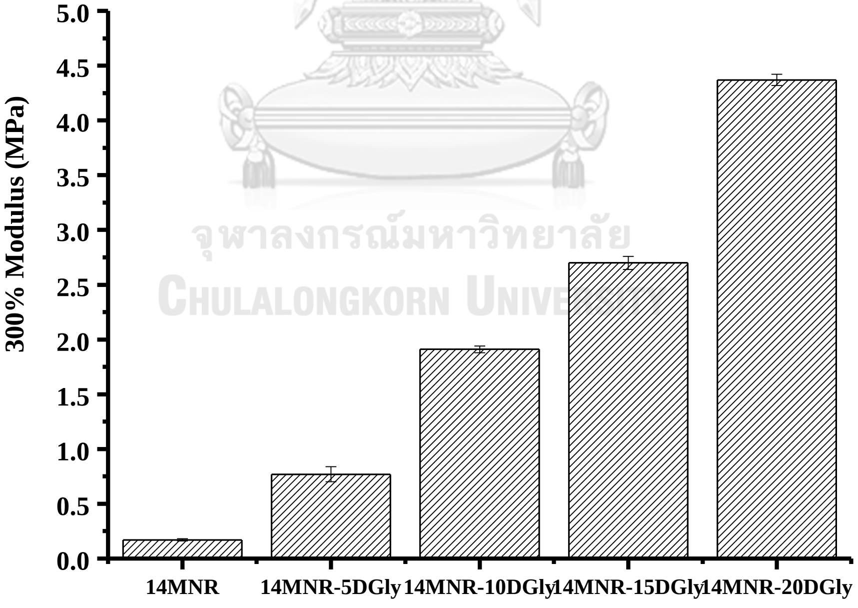


Figure 4.31 300% Modulus of thermorversible crosslinking 14MNR with different amounts of diethylene glycol

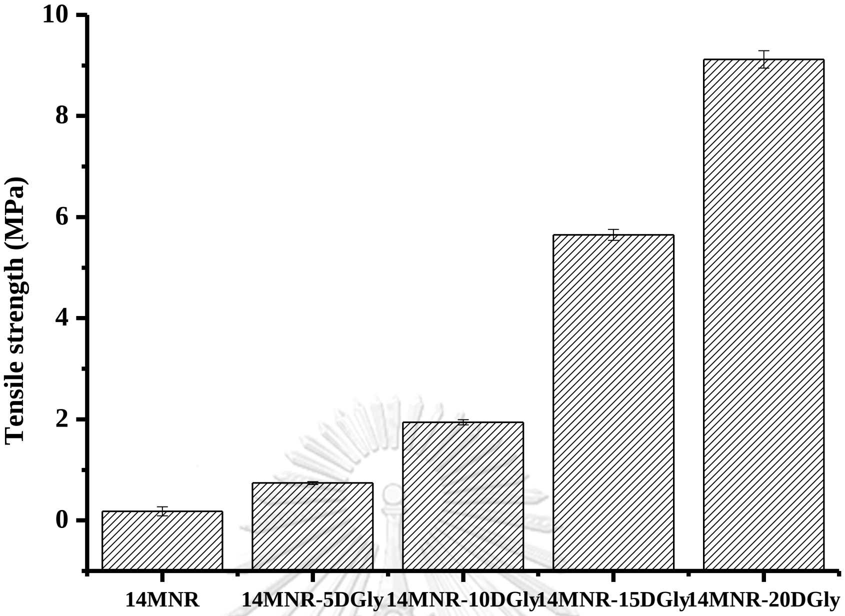


Figure 4.32 Tensile strength of thermoreversible crosslinking 14MNR with different amounts of diethylene glycol

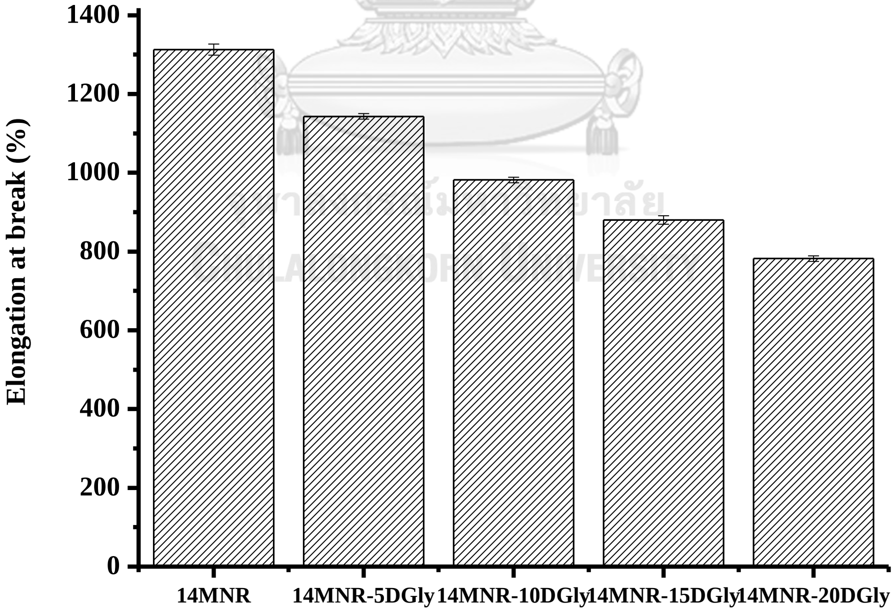


Figure 4.33 Elongation at break (%) of thermoreversible crosslinking 14MNR with different amounts of diethylene glycol

4.4.5 Reprocessability of Thermoreversible Crosslinking MNR with Diethylene Glycol

The reprocessability of the MNR crosslinked with diethylene glycol was also initially tested by cutting the sample into a small piece and remolded again at 150 °C. It was observed that at this temperature, the sample could be reshaped again. This indicated that the MNR crosslinking with diethylene glycol could be reprocessed at 150 °C. Reprocessability of the MNR crosslinked with diethylene glycol was also carried out with other methods as followed.

- *DSC thermogram of MNR Thermoreversible Crosslinking with Diethylene Glycol*

The thermoversible crosslinking of MNR with diethylene glycol was investigated from DSC thermogram as in Figure 4.34. The MNR premixed with 20 phr of diethylene glycol (14MNR-20DGly) was heated from 40 to 170 °C. It can be seen that the obtained heating curve showed the exothermal step-change at 90-140 °C. This indicated that there was the reaction between maleic hydride and hydroxyl groups of diethylene glycol. Thus, it led to the formation of the ester covalent crosslinking network[8]. On the other hand, the cooling curve was not observed any step-change. However, this exothermal step-change was not observed when heating the pure MNR. Moreover, after being treated by one to three heating-cooling cycles, DSC curves still showed exothermal step-changes at around the same position. This indicated that those broken ester thermoreversible covalent bonds can be reformed again. Thus, it can be inferred the MNR crosslinked with diethylene glycol can be reprocessed/or remolded.

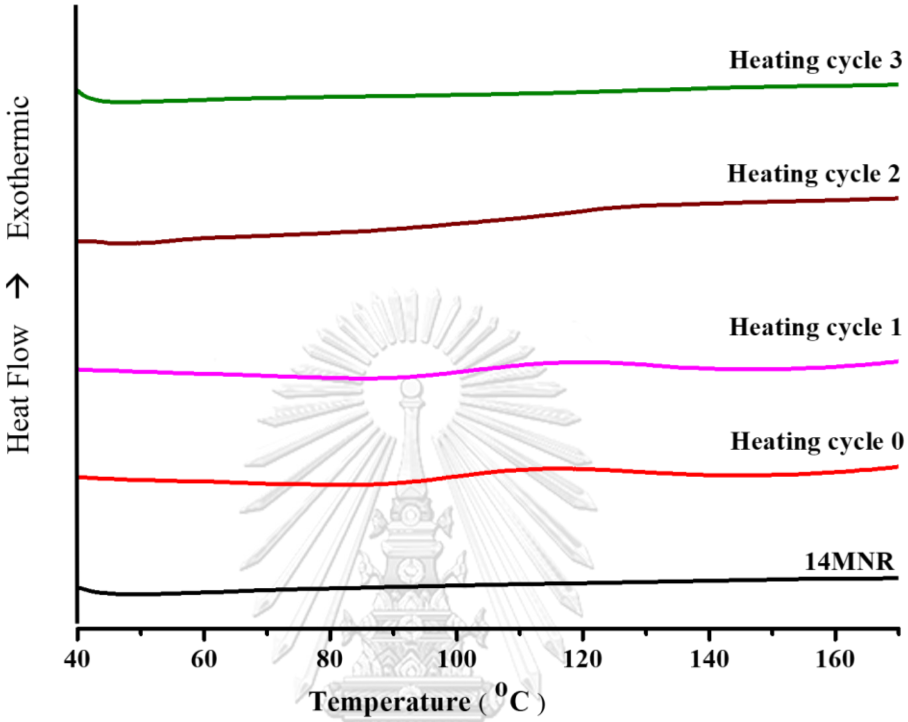


Figure 4.34 DSC curves of 14MNR-20DGly at the increment heating cycle

- FT-IR spectra of Thermoreversible Crosslinking MNR with Diethylene Glycol at the Increment Heating Cycle

The change in chemical structures during heating/cooling at 150/25 °C for 3 recycling times of 14MNR-20DGly was shown in Figure 4.35. It can be observed that when heating the sample to 150 °C, it caused the decrease in the intensity of the carboxylic acid band (1710 cm^{-1}). However, the increase in intensity of anhydride band (1790 cm^{-1}) was observed. This indicated that there was a conversion of the ester linkages to anhydride groups. However, during cooling down to 25 °C, the increase in the intensity of carboxylic acid band was found. The same behavior was also observed during the second and third heating/cooling cycle. This resulted also can confirm the thermoreversibility of the crosslink.

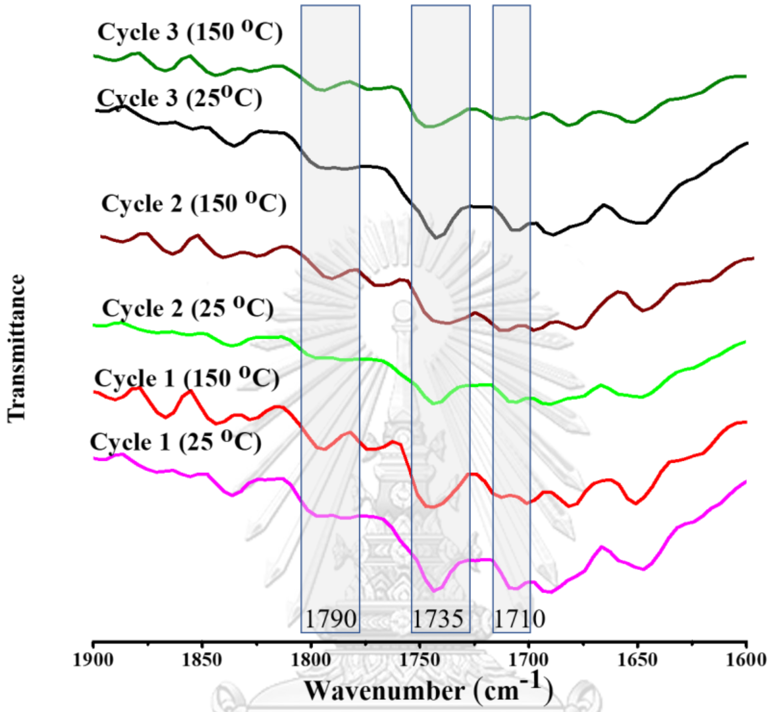


Figure 4.35 Realtime FT-IR spectrum of 14MNR-20DGly when heating to 150 °C at the increment heating-cooling cycle

- *Tensile Properties of Thermoreversible Crosslinking MNR with Diethylene Glycol at the Increment Heating Cycle*

The reprocessabilty of thermoreversible crosslinking MNR with diethylene glycol was also confirmed by tensile properties at increment recycling rounds as given in Table 4.11. Each property was depicted as a plot in Figure 4.36 to 4.39. After the first recycling, the tensile strength and modulus slightly decreases. The tensile strength was found to further decrease when increasing in round of recycling. However, after three rounds of recycling, the tensile strength of sample was still higher than the uncrosslinked MNR. Possibly, the deterioration of strength was not only due to the reduction of crosslinking density indicating by the lower modulus at increment recycling rounds but also the thermal degradation of rubber itself during remolding.

Table 4.11 Tensile properties of 14MNR-20Gly at increment recycling rounds.

Sample Name	**100% Modulus (MPa)**	**300% Modulus (MPa)**	**Tensile Strength (MPa)**	**Elongation at Break (%)**
14MNR-20DGly	3.96±0.04	4.37±0.05	9.12±0.17	782±7
Heating cycle1	3.33±0.10	3.67±0.07	7.71±0.11	697±11
Heating cycle2	2.23±0.06	2.62±0.08	4.46±0.10	629±7
Heating cycle3	1.39±0.07	1.76±0.07	3.12±0.08	507±9
14MNR	0.16±0.02	0.17±0.01	0.18±0.09	1313±14

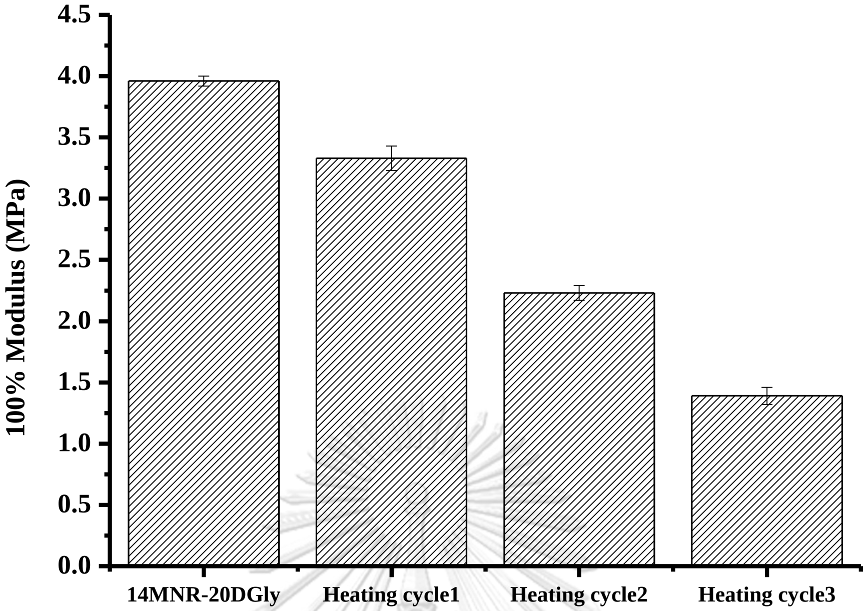


Figure 4.36 100% Modulus of 14MNR-20DGly at increment recycling round

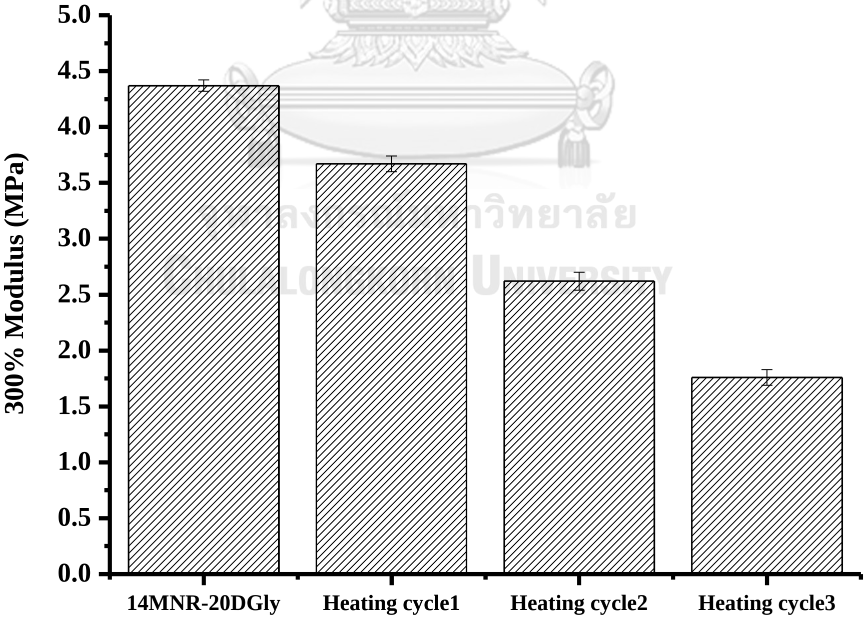


Figure 4.37 300% Modulus of 14MNR-20DGly at increment recycling round

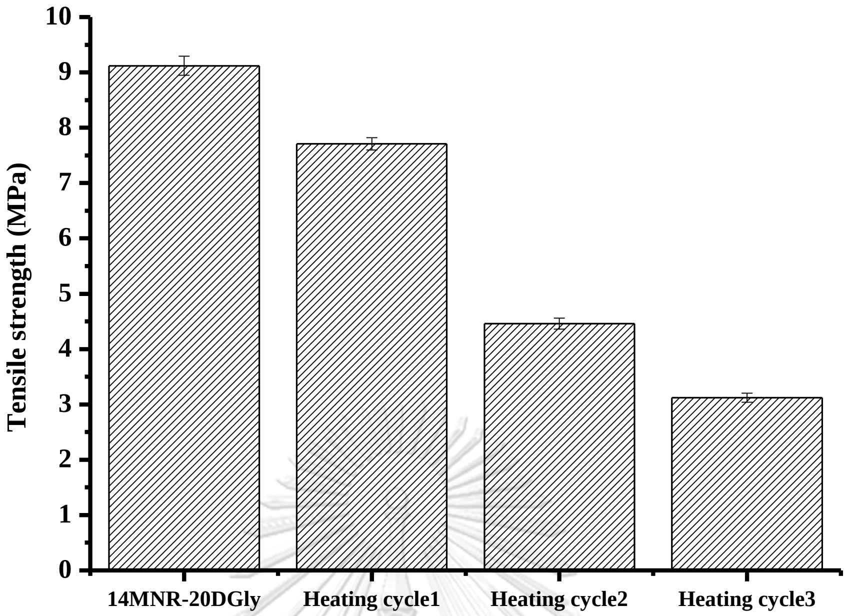


Figure 4.38 Tensile strength of 14MNR-20DGly at increment recycling round

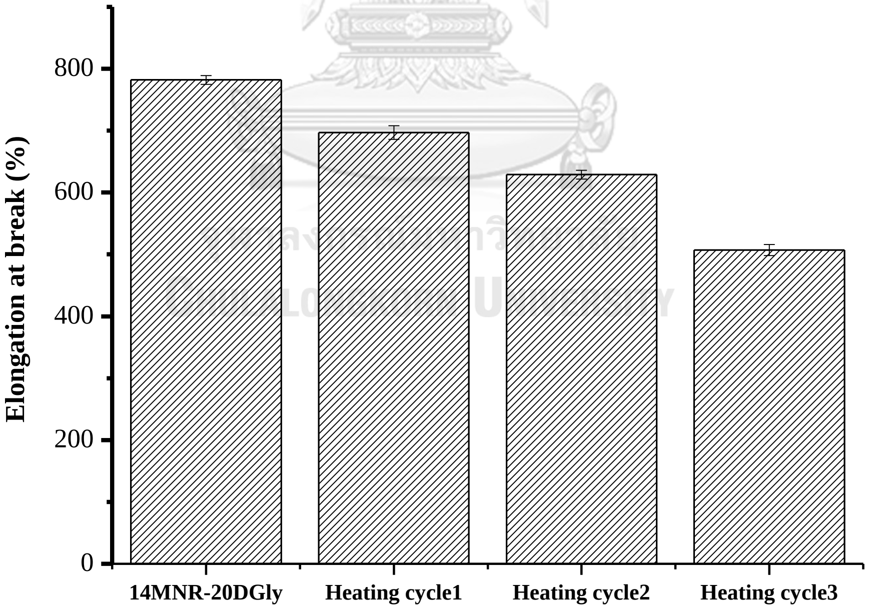


Figure 4.39 Elongation at break of 14MNR-20DGly at increment recycling round

4.5 Comparison Between Thermoreversible Crosslinking MNR with Glycerol and with Diethylene Glycol

In this part, the effect of thermoreversible crosslinking structure on the properties of the MNR was discussed. As mentioned earlier, diethylene glycol led to the formation of di-functional crosslinked structure which means there were two chains bond together. On the other hand, glycerol has three hydroxyl groups. Therefore, it can bond three rubber chains together, called as a tri-functional crosslinked structure.

- **Comparison in Swelling Index (%)**

From previous sections, the MNR can be crosslinked with both glycerol and diethylene glycol due to the reaction between the ring opening of succinic anhydride with the hydroxyl group of glycerol and diethylene glycol when heating up. However, when comparing the value of % swelling as shown in Figure 4.39, it was found that the MNR crosslinked with glycerol had higher % swelling than the one crosslinked with diethylene glycol. It meant the former one had lower crosslink density that the latter one. This might be due to the steric hindrance. From the chemical structure of glycerol, it can be seen that hydroxyl groups which acting as crosslinking site locates on each carbon atom. To form thermoreversible crosslink, when using glycerol as a crosslink agent, two/three rubber chains have to get closer than when using diethylene glycol, thus being more difficult. Therefore, this can lead to the lower crosslink density.

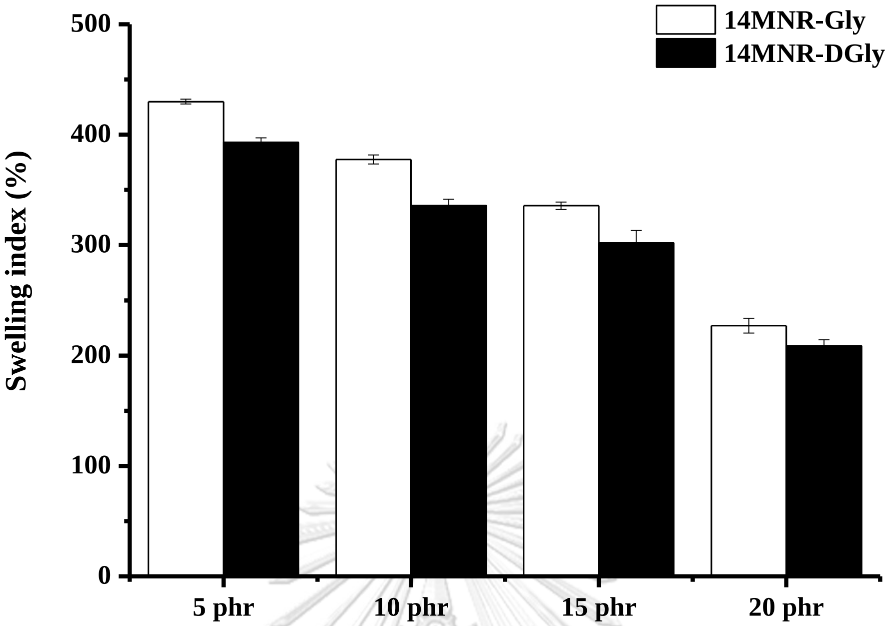


Figure 4.40 Comparison in swelling index (%) between 14MNR-Gly and 14MNR-DGly

- Comparison in Tensile Properties

Tensile properties of 14MNR crosslinked with glycerol were compared with those of 14MNR crosslinked with diethylene glycol in Figures 4.41 to 4.44. It can be seen that at the same amount of crosslinking agent the 100% modulus and 300% modulus of all 14MNR-DGly samples were higher than those of all 14MNR-Gly. This also indicated that the 14MNR-DGly samples had higher crosslinking density that the 14MNR-Gly samples. This caused the 14MNR-DGly in having higher tensile strength than the 14MNR-Gly as shown in Figure 4.43. However, due to the possessing of higher crosslinking density, it led the 14MNR-DGly to break at lower strain than the 14MNR-Gly.

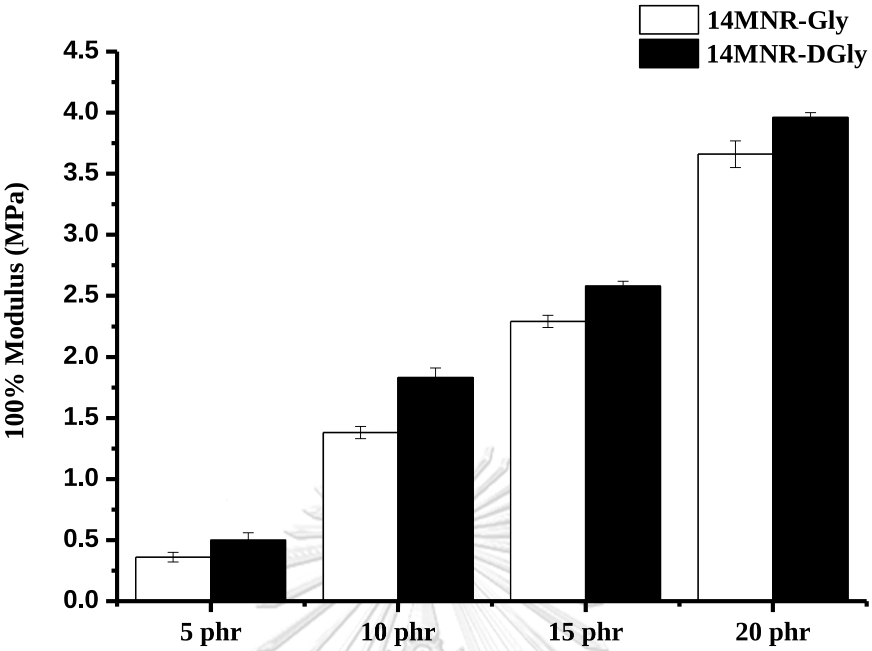


Figure 4.41 Comparison in 100% modulus between 14MNR-Gly and 14MNR-DGly

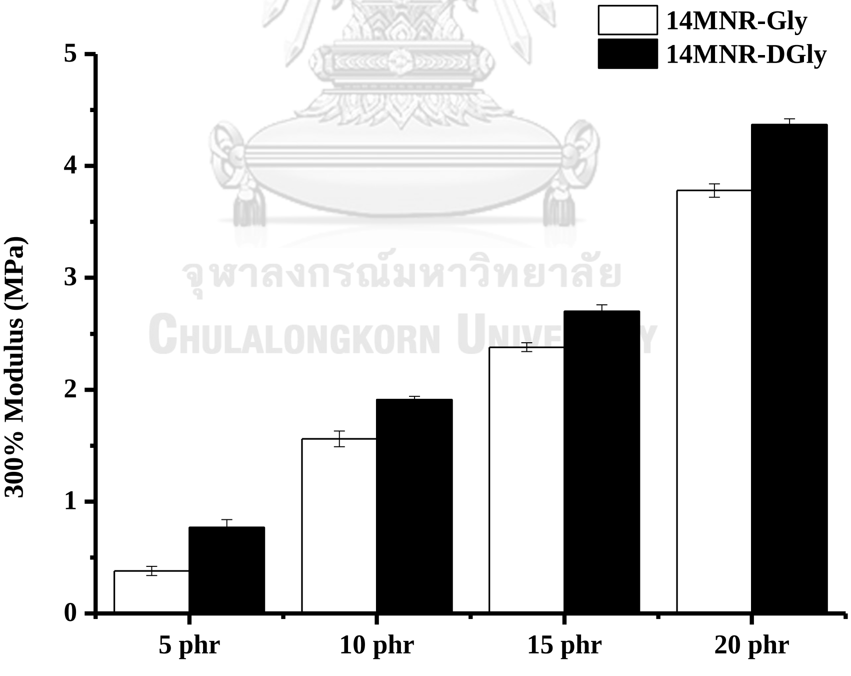


Figure 4.42 Comparison in 300% modulus between 14MNR-Gly and 14MNR-DGly

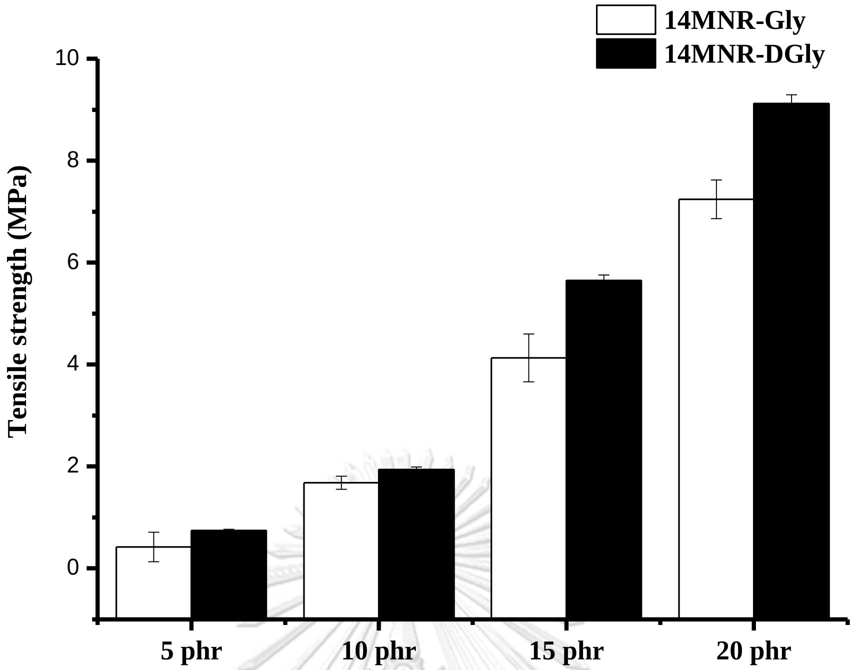


Figure 4.43 Comparison in tensile strength between 14MNR-Gly and 14MNR-DGly

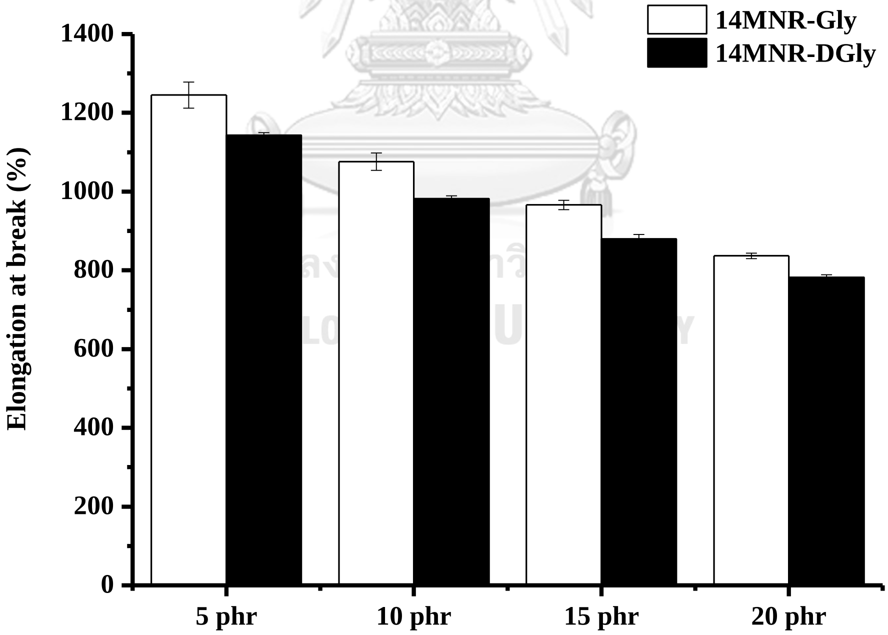


Figure 4.44 Comparison in % elongation at break between 14MNR-Gly and 14MNR-DGly

- Comparison in Reduction of Tensile Properties

In this section, the reduction in tensile properties of 14MNR-20Gly was compared with that of 14MNR-20DGly in Figures 4.45 to 4.48. It can be seen that diethylene glycol did not only give the MNR with higher modulus and tensile strength but also gave the MNR with higher thermal resistance. As seen in Figures 4.45 to 4.48, after recycling up to three rounds the reductions in modulus, tensile and elongation at break of the 14MNR crosslinked with diethylene glycol was mostly lower than those of the 14MNR crosslinked with glycerol.

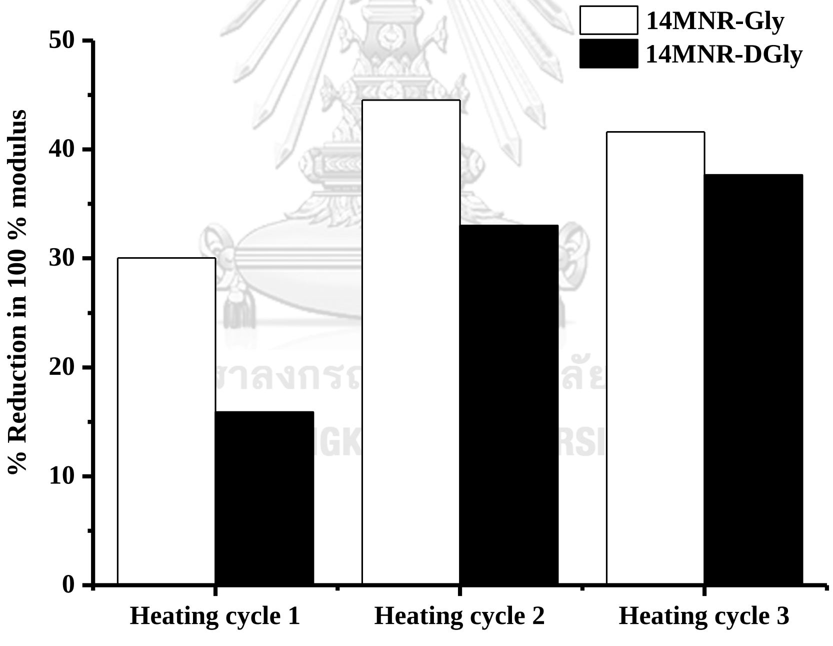


Figure 4.45 Comparison in reduction in 100% modulus between 14MNR-20Gly and 14MNR-20DGly

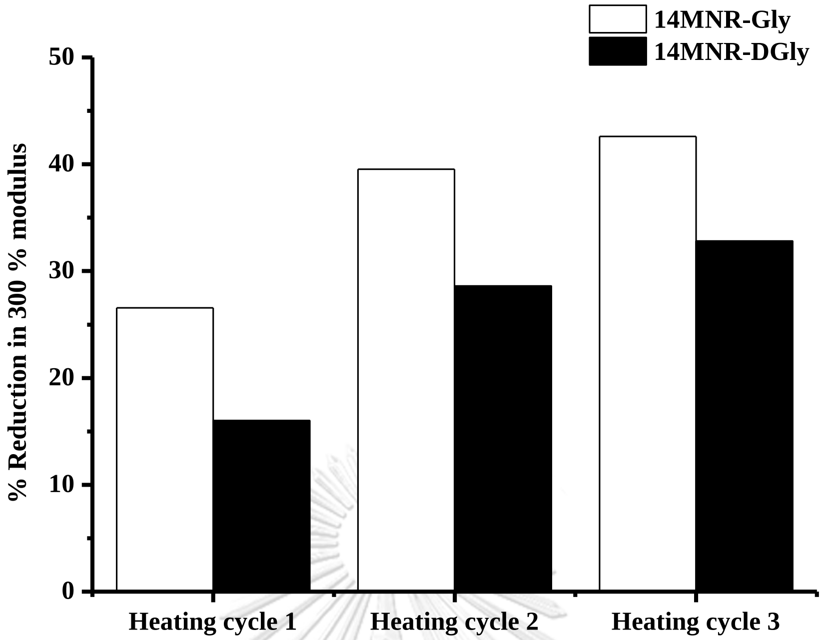


Figure 4.46 Comparison in reduction in 300% modulus between 14MNR-20Gly and 14MNR-20DGly

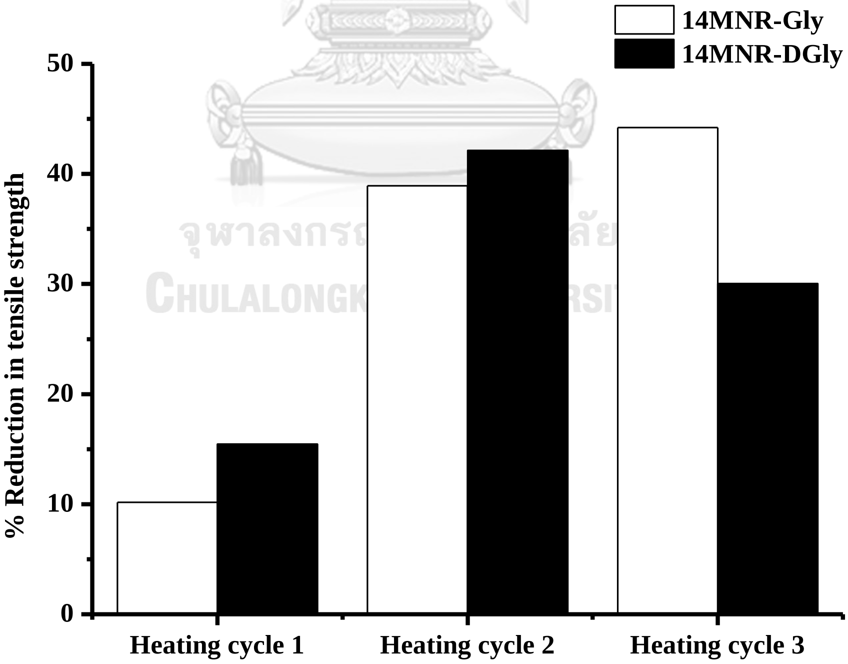


Figure 4.47 Comparison in reduction in tensile strength between 14MNR-20Gly and 14MNR-20DGly

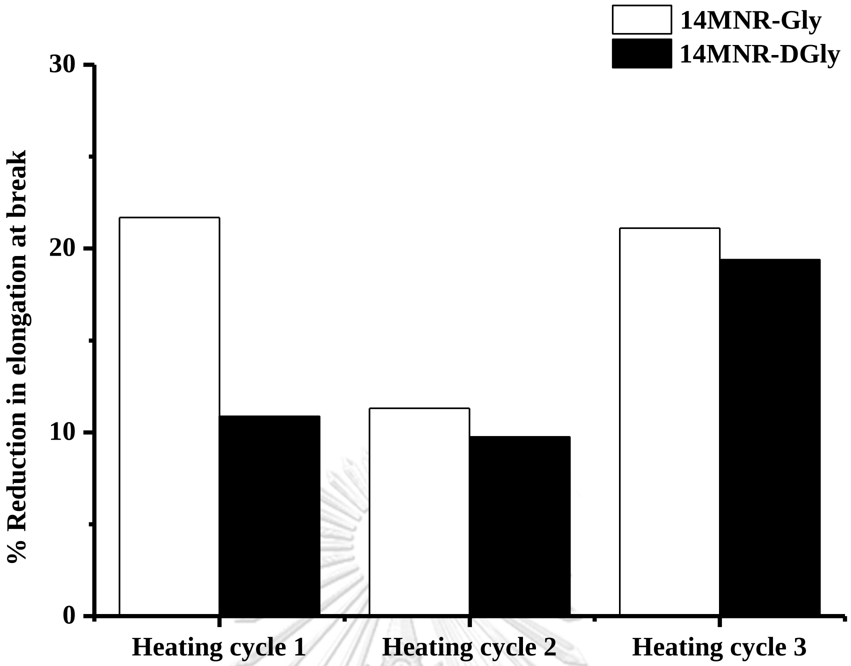


Figure 4.48 Comparison in reduction in % elongation at break between 14MNR-20Gly and 14MNR-20DGly

CHAPTER 5

CONCLUSIONS

This chapter summarized research contents in a novel crosslinking agent for ENR and NR. The study was divided in two parts. The first part is to investigate the possibility to use MA as a novel di-functional molecule for crosslinking ENR. The second part is to study prepare thermoreversibly crosslinking of NR. The glycerol and diethylene glycol were used as the crosslinking agents. The most important conclusion obtained in this thesis and the details are summarized below.

From the first part, the results showed that it was possible to thermally crosslink ENR with MA in the absence of catalyst. This can be confirmed by the decrease of swelling index (%), the improvement of tensile properties and thermal resistance. Degree of crosslinking was directly proportionally to the amount of MA. FT-IR spectra revealed that there were newly formed peaks represented the C=O stretching of ester group, indicating that the crosslinking of ENR by MA was introduced by a ring-opening of the oxirane ring with the succinic anhydride ring of MA. MDR rheographs indicated that the cure characteristic of ENR crosslinked with MA was marching behavior at the over cure zone. Moreover, the induction zone of curing was very short. Due to the abundant of oxirane rings which were active sites for crosslinking, the smooth rubber sheet of ENR50 cannot be obtained. The crosslinking was taken place too fast, leading the ENR50 to scorch. Although the tensile strength of ENR crosslinked with MA that obtained from this study was still lower than that crosslinked with sulfur, it was found that the crosslinking with MA was much active and also required none of another chemicals.

For the second part, it was found that the thermoreversible crosslinking of NR can be successfully obtained by heating the maleated NR with glycerol or diethylene glycol representing tri-functional and di-functional molecule, respectively. Initially, it was found that the MNR can be crosslinked by glycerol or diethylene glycol. This led to the decrease of swelling index (%), the improvement of tensile properties. Degree of crosslinking was directly proportionally to the amount of glycerol or diethylene glycol. From the FT-IR results, the occurrence of C=O stretching vibration of the ester and C=O stretching vibration of carboxyl groups indicated that the crosslinking was taken place by the reaction between MNR and hydroxyl groups of glycerol or diethylene glycol via the ring opening of MA grafted on the NR chains. The reprocessability of the MNR crosslinked with glycerol or diethylene glycol can be confirmed by remolding at 150 °C, thus giving a newly formed rubber sheet. Additionally, the reprocessability can also be supported by the recurrence of exothermal step-changes in DSC thermogram and also the change in the intensity of the carboxylic acid and anhydride band in FT-IR spectrum during heating-cooling cycles. Although the reprocessing/recycling led to the reduction in tensile properties, after 3 recycling the sample still possessed the tensile propertied that the uncrosslinked MNR. By comparing the swelling index (%) and tensile properties, it was noted that to use as a crosslinking agent for MNR diethylene glycol was superior to glycerol. This was attributed to the less steric hindrance effect, thus facilitating the crosslinking reaction.

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APPENDIX

Table A-1 Swelling index (%) of the crosslinking ENR with various MA content

Sample		ENR25	ENR50	1.0MA-ENR25	1.5MA-ENR25	2.0MA-ENR25	2.5MA-ENR25	3.0MA-ENR25	1.0MA-ENR50	1.5MA-ENR50	2.0MA-ENR50	2.5MA-ENR50	3.0MA-ENR50
W_0	1	0.2503	0.2506	0.2512	0.2498	0.2526	0.2496	0.2499	0.2505	0.2503	0.2497	0.2508	0.2506
	2	0.2499	0.2493	0.2521	0.2492	0.2511	0.2483	0.2489	0.2508	0.2505	0.2489	0.2495	0.2493
	3	0.2489	0.249	0.2527	0.2503	0.2513	0.2502	0.2511	0.2497	0.2499	0.2499	0.2501	0.2491
W_1	1	1.3290	1.2103	1.0851	1.0016	0.8916	0.7238	0.5897	0.5035	0.4455	0.3945	0.3360	0.2531
	2	1.2719	1.1916	1.1117	0.9693	0.9064	0.7250	0.6172	0.5668	0.4909	0.4206	0.3617	0.2318
	3	1.3465	1.1678	1.1245	0.9461	0.8770	0.7455	0.6553	0.5443	0.4573	0.3698	0.3026	0.2914
Swelling index (%)	1	531	483	432	401	353	290	236	201	178	158	134	101
	2	509	478	441	389	361	292	248	226	196	169	145	93
	3	541	469	445	378	349	298	261	218	183	148	121	117
average		527	477	439	389	354	293	248	215	186	158	133	104
S.D.		16	7	6	12	6	4	13	13	9	11	12	12

Table A-2 100 % modulus (MPa) of crosslinked ENR25 compared with uncrosslinked ENR25

Sample	Uncrosslinked	1.0MA-ENR25	1.5MA-ENR25	2.0MA-ENR25	2.5MA-ENR25	3.0MA-ENR25
1	0.14	N/A	0.75	1.26	1.35	1.18
2	0.17	N/A	0.76	1.14	1.24	1.31
3	0.19	N/A	0.80	1.21	1.13	1.29
4	0.15	N/A	0.85	1.13	1.14	1.17
5	0.13	N/A	0.84	1.29	1.16	1.23
average	0.16	N/A	0.80	1.21	1.22	1.24
S.D.	0.04	N/A	0.09	0.14	0.21	0.28

Table A-3 300 % modulus (MPa) of crosslinked ENR25 compared with uncrosslinked ENR25

Sample	Uncrosslinked	1.0MA-ENR25	1.5MA-ENR25	2.0MA-ENR25	2.5MA-ENR25	3.0MA-ENR25
1	0.16	N/A	1.72	2.05	2.63	2.64
2	0.19	N/A	1.78	1.9	2.52	2.78
3	0.2	N/A	1.84	1.92	2.54	2.74
4	0.17	N/A	1.86	2.04	2.62	2.68
5	0.16	N/A	1.85	1.99	2.56	2.73
average	0.18	N/A	1.80	1.98	2.58	2.71
S.D.	0.02	N/A	0.12	0.27	0.39	0.32

Table A-4 tensile strength (MPa) of crosslinked ENR25 compared with uncrosslinked ENR25

Sample	Uncrosslinked	1.0MA-ENR25	1.5MA-ENR25	2.0MA-ENR25	2.5MA-ENR25	3.0MA-ENR25
1	0.39	N/A	3.39	6.7	6.95	7.8
2	0.35	N/A	3.48	6.75	7.12	8.01
3	0.48	N/A	3.49	6.61	6.93	7.96
4	0.44	N/A	3.41	6.58	6.99	7.88
5	0.4	N/A	3.38	6.8	6.92	7.89
average	0.42	N/A	3.44	6.67	6.95	7.90
S.D.	0.11	N/A	0.21	0.48	0.36	0.57

Table A-5 elongation at break (%) of crosslinked ENR25 compared with uncrosslinked ENR25

Sample	Uncrosslinked	1.0MA-ENR25	1.5MA-ENR25	2.0MA-ENR25	2.5MA-ENR25	3.0MA-ENR25
1	1515	N/A	652	575	487	469
2	1568	N/A	624	542	471	435
3	1544	N/A	648	539	489	472
4	1580	N/A	621	549	469	454
5	1512	N/A	630	567	477	448
average	1544	N/A	635	554	478	456
S.D.	121	N/A	43	53	32	47

Table A-6 % Grafting of 10MNR when varying processing condition

Condition			MA 10 phr				
Mastication time (min)	Reaction time (min)	Reaction Temperature(°C)	1	2	3	average	S.D.
3	10	140	0.37	0.25	0.37	0.32	0.07
5	10	140	0.98	0.86	0.86	0.90	0.07
7	10	140	0.86	0.74	0.74	0.78	0.07
3	15	140	1.10	0.98	1.10	1.06	0.07
5	15	140	1.10	1.23	1.23	1.18	0.07
7	15	140	0.98	0.98	1.10	1.02	0.07
3	20	140	0.98	1.11	1.35	1.14	0.18
5	20	140	1.23	1.35	1.47	1.35	0.12
7	20	140	0.98	1.11	1.23	1.10	0.12
3	10	150	0.86	0.98	0.98	0.94	0.07
5	10	150	1.11	1.11	0.98	1.06	0.07
7	10	150	0.98	0.98	1.10	1.02	0.07
3	15	150	0.98	1.10	1.35	1.14	0.19
5	15	150	1.23	1.23	1.47	1.31	0.14
7	15	150	1.10	1.10	0.98	1.06	0.07
3	20	150	0.98	1.10	0.98	1.02	0.07
5	20	150	0.86	1.10	0.98	0.98	0.12
7	20	150	0.74	0.86	1.10	0.90	0.18
3	10	160	0.74	0.36	0.25	0.45	0.25
5	10	160	0.49	0.61	0.61	0.57	0.07
7	10	160	0.37	0.98	0.97	0.77	0.35
3	15	160	0.61	0.61	0.74	0.65	0.07
5	15	160	0.98	0.98	1.10	1.02	0.07
7	15	160	0.98	0.86	0.98	0.94	0.07
3	20	160	0.86	0.86	0.74	0.82	0.07
5	20	160	0.98	0.74	0.98	0.90	0.14
7	20	160	0.61	0.74	0.61	0.65	0.07

Table A-7 % Grafting of 12MNR when varying processing condition

Condition			MA 12 phr				
Mastication time (min)	Reaction time (min)	Reaction Temperature (°C)	1	2	3	average	S.D.
3	10	140	0.61	0.61	0.61	0.61	0
5	10	140	0.61	0.98	1.10	0.88	0.26
7	10	140	0.98	1.10	0.85	0.88	0.12
3	15	140	1.35	1.47	1.35	1.25	0.07
5	15	140	1.35	1.60	1.47	1.38	0.12
7	15	140	1.35	1.47	1.71	1.32	0.19
3	20	140	0.98	1.10	0.98	1.10	0.07
5	20	140	1.59	1.59	1.71	1.54	0.07
7	20	140	1.10	1.10	0.98	1.10	0.07
3	10	150	1.23	1.47	1.35	1.35	0.12
5	10	150	1.47	1.47	1.60	1.51	0.07
7	10	150	1.47	1.47	1.47	1.47	0
3	15	150	1.47	1.59	1.71	1.59	0.12
5	15	150	1.47	1.47	1.35	1.42	0.07
7	15	150	1.47	1.35	1.23	1.34	0.12
3	20	150	1.47	1.47	1.35	1.43	0.07
5	20	150	1.35	1.47	1.47	1.43	0.07
7	20	150	1.35	1.23	1.35	1.31	0.07
3	10	160	0.74	0.74	0.61	0.69	0.07
5	10	160	0.98	0.98	1.10	1.02	0.07
7	10	160	1.23	1.10	1.10	1.14	0.07
3	15	160	0.86	0.86	0.98	0.90	0.07
5	15	160	1.23	1.35	1.35	1.31	0.07
7	15	160	1.23	1.23	1.23	1.23	0
3	20	160	1.23	1.35	1.35	1.31	0.07
5	20	160	1.23	1.23	1.10	1.18	0.07
7	20	160	0.98	0.86	0.98	0.94	0.07

Table A-8 % Grafting of 14MNR when varying processing condition

Condition			MA 14 phr				
Mastication time (min)	Reaction time (min)	Reaction Temperature (°C)	1	2	3	average	S.D.
3	10	140	0.61	0.74	0.74	0.69	0.07
5	10	140	0.98	1.10	1.10	1.06	0.07
7	10	140	1.23	1.35	1.10	1.23	0.12
3	15	140	1.47	1.47	1.35	1.43	0.07
5	15	140	1.60	1.47	1.72	1.59	0.12
7	15	140	1.59	1.59	1.59	1.59	0
3	20	140	1.59	1.72	1.72	1.67	0.07
5	20	140	1.59	1.71	1.59	1.63	0.07
7	20	140	1.35	1.47	1.35	1.39	0.07
3	10	150	1.23	1.47	1.35	1.35	0.12
5	10	150	1.47	1.47	1.59	1.51	0.07
7	10	150	1.47	1.47	1.47	1.47	0
3	15	150	1.47	1.59	1.72	1.59	0.12
5	15	150	1.84	1.72	1.72	1.76	0.07
7	15	150	1.59	1.59	1.59	1.59	0
3	20	150	1.47	1.47	1.47	1.47	0
5	20	150	1.35	1.35	1.47	1.39	0.07
7	20	150	1.35	1.72	1.35	1.47	0.21
3	10	160	0.86	0.86	0.86	0.86	0
5	10	160	1.10	0.98	1.22	1.10	0.12
7	10	160	1.35	1.35	1.47	1.39	0.07
3	15	160	1.10	1.59	1.47	1.39	0.26
5	15	160	1.47	1.59	1.47	1.51	007
7	15	160	1.47	1.47	1.47	1.47	0
3	20	160	1.47	1.35	1.35	1.39	0.07
5	20	160	1.47	1.23	1.10	1.27	0.19
7	20	160	1.23	1.10	1.10	1.14	0.07

Table A-9 Swelling index (%) of thermoreversible crosslinking MNR with different amounts of glycerol

Sample		14MNR	14MNR-5Gly	14MNR-10Gly	14MNR-15Gly	14MNR-20Gly
W_0	1	0.2512	0.25	0.2498	0.2505	0.25
	2	0.2502	0.2506	0.2504	0.2503	0.2509
	3	0.2508	0.2501	0.2509	0.2507	0.2512
W_1	1	1.5072	1.3198	1.187	1.0908	0.8281
	2	1.498	1.334	1.1903	1.0825	0.8302
	3	1.5026	1.3248	1.2101	1.1012	0.8024
Swelling index (%)	1	500	527.92	475.18	435.45	331.24
	2	498.72	532.32	475.36	432.48	330.89
	3	499.12	529.71	482.30	439.25	319.43
average		499.28	529.98	477.61	435.73	327.19
S.D.		0.65	2.21	4.06	3.39	6.72

Table A-10 100 % modulus (MPa) of thermoreversible crosslinking 14MNR with different amounts of glycerol

Sample	14MNR	14MNR-5Gly	14MNR-10Gly	14MNR-15Gly	14MNR-20Gly
1	0.16	0.32	1.34	2.27	3.63
2	0.14	0.37	1.43	2.29	3.62
3	0.17	0.35	1.36	2.35	3.78
4	0.18	0.40	1.35	2.25	3.57
5	0.13	0.33	1.38	2.30	3.63
average	0.16	0.36	1.38	2.29	3.66
S.D.	0.03	0.40	0.45	0.05	0.11

Table A-11 300 % modulus (MPa) of thermoreversible crosslinking 14MNR with different amounts of glycerol

Sample	14MNR	14MNR-5Gly	14MNR-10Gly	14MNR-15Gly	14MNR-20Gly
1	0.18	0.39	1.58	2.36	3.72
2	0.17	0.34	1.60	2.42	3.84
3	0.16	0.36	1.49	2.35	3.82
4	0.15	0.41	1.52	2.43	3.75
5	0.17	0.37	1.63	2.39	3.79
average	0.17	0.38	1.57	2.38	3.78
S.D.	0.01	0.03	0.07	0.04	0.06

Table A-12 Tensile strength (MPa) of thermoreversible crosslinking 14MNR with different amounts of glycerol

Sample	14MNR	14MNR-5Gly	14MNR-10Gly	14MNR-15Gly	14MNR-20Gly
1	0.18	0.41	1.78	4.03	7.25
2	0.19	0.39	1.69	4.07	7.22
3	0.17	0.38	1.68	4.13	7.21
4	0.18	0.41	1.76	4.01	7.24
5	0.17	0.42	1.72	4.08	7.23
average	0.18	0.40	1.74	4.06	7.23
S.D.	0.09	0.02	0.05	0.06	0.02

Table A-13 Elongation at break (%) of thermoreversible crosslinking 14MNR with different amounts of glycerol

Sample	14MNR	14MNR-5Gly	14MNR-10Gly	14MNR-15Gly	14MNR-20Gly
1	1327	1211	1072	954	832
2	1305	1245	1100	978	835
3	1298	1278	1065	965	846
4	1309	1235	1056	970	840
5	1314	1261	1084	963	833
average	1313	1245	1076	967	837
S.D.	14.53	33.50	22.27	12.01	7.81

Table A-14 100 % modulus (MPa) of 14MNR-20Gly at increment recycling round

Sample	14MNR-20Gly	Heating cycle1	Heating cycle2	Heating cycle3
1	3.63	2.38	1.38	0.78
2	3.62	2.42	1.35	0.83
3	3.78	2.48	1.36	0.85
4	3.57	2.54	1.39	0.89
5	3.63	2.46	1.38	0.92
average	3.66	2.47	1.37	0.86
S.D.	0.11	0.08	0.02	0.07

Table A-15 300 % modulus (MPa) of 14MNR-20Gly at increment recycling round

Sample	14MNR-20Gly	Heating cycle1	Heating cycle2	Heating cycle3
1	3.72	2.57	1.57	0.97
2	3.84	2.65	1.56	0.89
3	3.82	2.83	1.64	0.92
4	3.75	2.72	1.72	0.94
5	3.79	2.64	1.58	0.93
average	3.78	2.68	1.62	0.93
S.D.	0.06	0.13	0.09	0.04

Table A-16 Tensile strength (MPa) of 14MNR-20Gly at increment recycling round

Sample	14MNR-20Gly	Heating cycle1	Heating cycle2	Heating cycle3
1	7.25	6.21	3.85	2.17
2	7.22	6.56	3.94	2.02
3	7.21	6.28	3.89	2.08
4	7.24	6.34	3.91	2.32
5	7.23	6.38	3.87	2.21
average	7.23	6.37	3.89	2.17
S.D.	0.02	0.18	0.05	0.15

Table A-17 Elongation at break (%) of 14MNR-20Gly at increment recycling round

Sample	14MNR-20Gly	Heating cycle1	Heating cycle2	Heating cycle3
1	832	757	679	531
2	835	765	698	538
3	846	763	683	545
4	840	768	680	540
5	833	783	670	537
average	837	768	682	538
S.D.	7.81	13.32	14.30	7

Table A-18 Swelling index (%) of thermoreversible crosslinking MNR with different amounts of diethylene glycol

Sample		14MNR	14MNR-5DGly	14MNR-10DGly	14MNR-15DGly	14MNR-20DGly
W_0	1	0.2512	0.2513	0.2508	0.2511	0.2501
	2	0.2502	0.2568	0.2487	0.2509	0.2514
	3	0.2508	0.2492	0.2499	0.2496	0.2502
W_1	1	1.5072	1.2467	1.0878	0.9789	0.7631
	2	1.498	1.2541	1.1004	1.0126	0.7924
	3	1.5026	1.2329	1.0782	1.0294	0.7642
Swelling index (%)	1	500	396.10	333.73	289.84	205.12
	2	498.72	388.36	342.46	303.59	215.19
	3	499.12	394.74	331.45	312.42	205.44
average		499.28	393.07	355.88	301.95	208.58
S.D.		0.65	4.14	5.81	11.38	5.73

Table A-19 100 % modulus (MPa) of thermoreversible crosslinking 14MNR with different amounts of diethylene glycol

Sample	14MNR	14MNR-5DGly	14MNR-10DGly	14MNR-15DGly	14MNR-20DGly
1	0.16	0.49	1.72	2.52	3.91
2	0.14	0.42	1.89	2.58	3.94
3	0.17	0.58	1.91	2.63	4.01
4	0.18	0.47	1.86	2.57	3.98
5	0.13	0.52	1.79	2.59	3.96
average	0.16	0.50	1.83	2.58	3.96
S.D.	0.03	0.06	0.08	0.04	0.04

Table A-20 300 % modulus (MPa) of thermoreversible crosslinking 14MNR with different amounts of diethylene glycol

Sample	14MNR	14MNR-5DGly	14MNR-10DGly	14MNR-15DGly	14MNR-20DGly
1	0.18	0.71	1.94	2.78	4.36
2	0.17	0.88	1.87	2.69	4.27
3	0.16	0.73	1.91	2.63	4.41
4	0.15	0.82	1.93	2.74	4.35
5	0.17	0.73	1.89	2.67	4.39
average	0.17	0.77	1.91	2.70	4.36
S.D.	0.01	0.07	0.03	0.06	0.05

Table A-21 Tensile strength (MPa) of thermoreversible crosslinking 14MNR with different amounts of diethylene glycol

Sample	14MNR	14MNR-5DGly	14MNR-10DGly	14MNR-15DGly	14MNR-20DGly
1	0.18	0.78	1.96	5.46	9.32
2	0.19	0.72	1.97	5.64	9.01
3	0.17	0.74	1.99	5.73	8.88
4	0.18	0.76	1.87	5.69	9.21
5	0.17	0.71	1.89	5.71	9.18
average	0.18	0.74	1.94	5.65	9.12
S.D.	0.09	0.03	0.05	0.11	0.17

Table A-22 Elongation at break (%) of thermoreversible crosslinking 14MNR with different amounts of diethylene glycol

Sample	14MNR	14MNR-5DGly	14MNR-10DGly	14MNR-15DGly	14MNR-20DGly
1	1327	1152	973	892	773
2	1305	1136	982	873	791
3	1298	1147	991	865	786
4	1309	1140	984	883	779
5	1314	1139	978	887	782
average	1313	1143	982	880	782
S.D.	14.53	6.53	6.73	10.91	6.83

Table A-23 100 % modulus (MPa) of 14MNR-20DGly at increment recycling round

Sample	14MNR-20DGly	Heating cycle1	Heating cycle2	Heating cycle3
1	3.91	3.45	2.15	1.35
2	3.94	3.38	2.23	1.43
3	4.01	3.21	2.19	1.30
4	3.98	3.26	2.31	1.39
5	3.96	3.36	2.28	1.47
average	3.96	3.33	2.32	1.39
S.D.	0.04	0.10	0.06	0.07

Table A-24 300 % modulus (MPa) of 14MNR-20DGly at increment recycling round.

Sample	14MNR-20DGly	Heating cycle1	Heating cycle2	Heating cycle3
1	4.36	3.58	2.58	1.73
2	4.27	3.69	2.64	1.84
3	4.41	3.71	2.72	1.82
4	4.35	3.64	2.52	1.68
5	4.39	3.75	2.66	1.75
average	4.36	3.68	2.62	1.76
S.D.	0.05	0.07	0.08	0.66

Table A-25 Tensile strength (MPa) of 14MNR-20DGly at increment recycling round.

Sample	14MNR-20DGly	Heating cycle1	Heating cycle2	Heating cycle3
1	9.32	7.56	4.31	3.01
2	9.01	7.63	4.52	3.21
3	8.88	7.82	4.58	3.12
4	9.21	7.74	4.43	3.17
5	9.18	7.79	4.48	3.08
average	9.12	7.71	4.46	3.12
S.D.	0.17	0.11	0.10	0.08

Table A-26 Elongation at break (%) of 14MNR-20DGly at increment recycling round.

Sample	14MNR-20DGly	Heating cycle1	Heating cycle2	Heating cycle3
1	773	701	625	498
2	791	692	638	506
3	786	711	629	511
4	779	683	620	502
5	782	698	635	521
average	782	697	630	508
S.D.	6.83	10.41	7.30	8.90

Table A-27 Comparison in reduction in 100% modulus between 14MNR-20Gly and 14MNR-20DGly

Sample		M_{100} (MPa)	% Residual	% Reduction
14MNR-20Gly	Heating cycle0	3.53	-	-
	Heating cycle1	2.47	69.97	30.03
	Heating cycle2	1.37	55.47	44.53
	Heating cycle3	0.8	58.39	41.61
14MNR-20DGly	Heating cycle0	3.96	-	-
	Heating cycle1	3.33	84.09	15.91
	Heating cycle2	2.23	66.97	33.03
	Heating cycle3	1.39	62.33	37.67

Table A-28 Comparison in reduction in 300% modulus between 14MNR-20Gly and 14MNR-20DGly

Sample		M_{300} (MPa)	% Residual	% Reduction
14MNR-20Gly	Heating cycle0	3.65	-	-
	Heating cycle1	2.68	73.42	26.58
	Heating cycle2	1.62	60.45	39.55
	Heating cycle3	0.93	57.41	42.59
14MNR-20DGly	Heating cycle0	4.37	-	-
	Heating cycle1	3.67	83.98	16.02
	Heating cycle2	2.62	71.39	28.61
	Heating cycle3	1.76	67.18	32.82

Table A-29 Comparison in reduction in tensile strength between 14MNR-20Gly and 14MNR-20DGly

Sample		Tensile strength (MPa)	% Residual	% Reduction
14MNR-20Gly	Heating cycle0	7.09	-	-
	Heating cycle1	6.37	89.84	10.16
	Heating cycle2	3.89	61.07	38.93
	Heating cycle3	2.17	55.78	44.22
14MNR-20DGly	Heating cycle0	9.12	-	-
	Heating cycle1	7.71	84.54	15.46
	Heating cycle2	4.46	57.85	42.15
	Heating cycle3	3.12	69.96	30.04

Table A-30 Comparison in reduction in % elongation at break between 14MNR-20Gly and 14MNR-20DGly

Sample		% elongation at break	% Residual	% Reduction
14MNR-20Gly	Heating cycle0	982	-	-
	Heating cycle1	769	78.31	21.69
	Heating cycle2	682	88.69	11.31
	Heating cycle3	538	78.89	21.11
14MNR-20DGly	Heating cycle0	782	-	-
	Heating cycle1	697	89.13	10.87
	Heating cycle2	629	90.24	9.76
	Heating cycle3	507	80.60	19.40

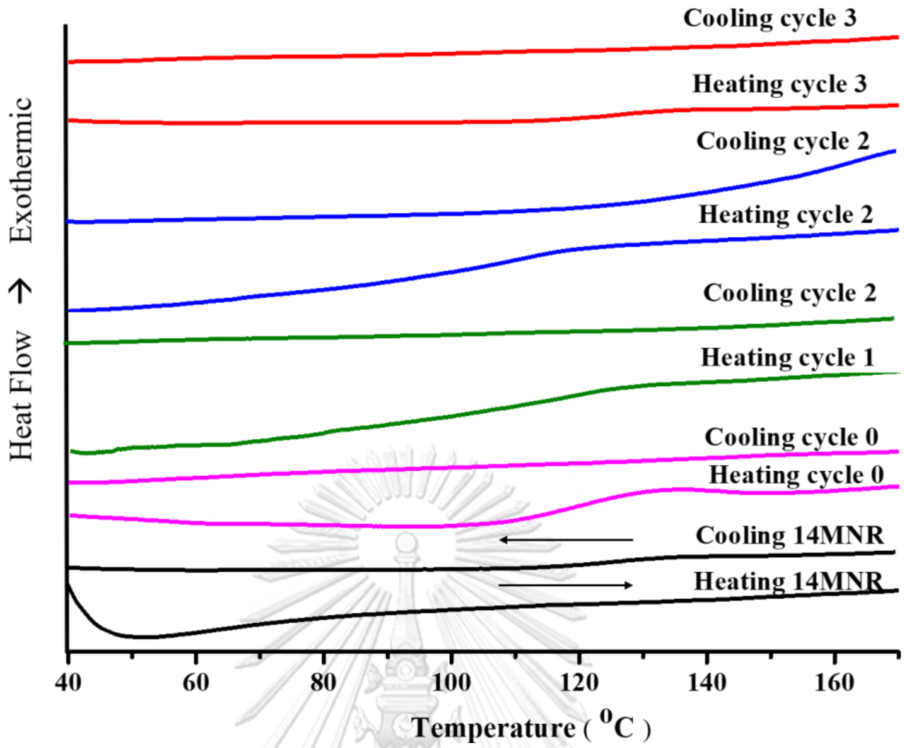

Figure A-1 DSC curves of 14MNR-20Gly at the increment heating-cooling cycle

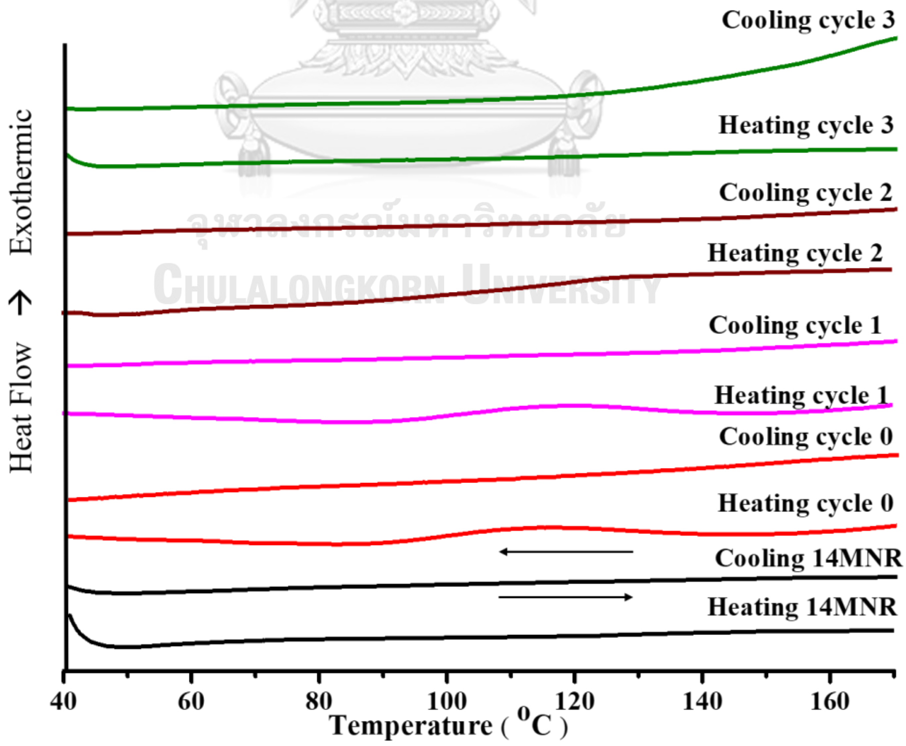

Figure A-2 DSC curves of 14MNR-20DGly at the increment heating-cooling cycle

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