A NEW CROSSLINKING METHOD OF ISOBUTYLENE-ISOPRENE COPOLYMER

A Thesis
Presented to
The Graduate Faculty at The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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May, 2019

A NEW CROSSLINKING METHOD OF ISOBUTYLENE-ISOPRENE COPOLYMER

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Thesis

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ABSTRACT

Polyisobutylene is unique among amorphous polymers in the sense that it has low gas permeability. Isobutylene-isoprene rubber (IIR) contains a small amount to isoprene to allow crosslinking through the unsaturated C=C bonds of the isoprene units. Traditional crosslinking methods of IIR include sulfur vulcanization and phenolic resin vulcanization. Peroxides induce chain scission reaction of IIR and cannot be used to crosslink IIR.

In this study, a new peroxide curable IIR derivative has been synthesized via Alder-ene reaction. The introduction of trimethylolpropane trimethacrylate (TMPTMA) successfully suppress the chain scission reaction. The crosslink behavior of this new modified IIR with various loadings of trimethylolpropane trimethacrylate (TMPTMA) as coagent and benzoyl peroxide (BPO) has been studied. The cross-link density is measured by the equilibrium–swelling technique. The crosslinking mechanisms are studied using a model compound synthesized from ethyl propiolate and 2-methyl-2-butylene. The coagent TMPTMA not only promote cure and prevent chain scission but also form segregated domains that likely provide reinforcement to the continuous rubber phase. Hence, the new peroxide vulcanized IIR has both greater tensile strength and elongation compared with traditional sulfur cured IIR and bromobutyl rubber.

ACKNOWLEDGEMENTS

I am sincerely grateful to my advisor Dr. Li Jia for his patience and guidance throughout my master career. All the achievements I made depend on your mentorship. I would also like to thank Dr. Yu Zhu for our discussions and being on my committee. I am grateful to my family for financial support. I must thank my group members Xuesong Yan, Yihong Zhao, Yu sun, Yiwei Dai, Nathan Schmitz, Honghe Liang, Linhui Zhu and former group members Mengsha Qian and Shiyu He. I also want to thank those people who help me with my research.

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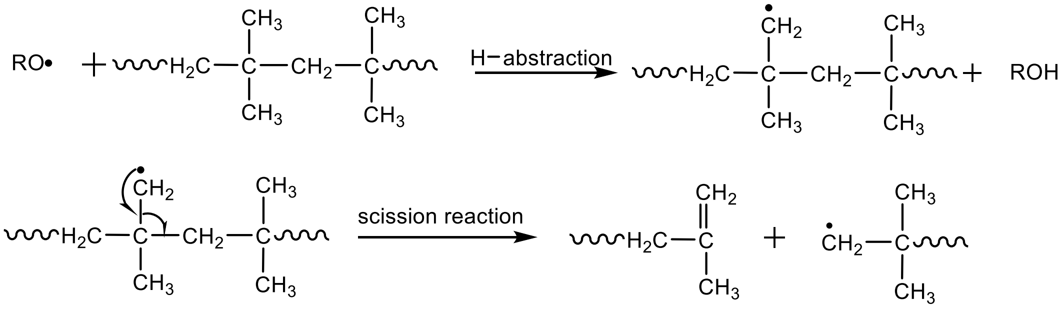
CHAPTER I

INTRODUCTION OF BUTYL RUBBER CROSSLINKING

1.1 General description of isobutylene rich elastomers

Polyisobutylene, also known as PIB, is valued for its good chemical resistance, vibration dampening ability, and superior air permeability. It was first discovered by BASF in 1931 via a boron trifluoride catalyst at low temperatures. However, unlike other unsaturated elastomer, polyisobutylene (PIB) cannot be crosslinked by traditional used vulcanization system such as sulfur-accelerator system and peroxide system. The former is because of the saturate chain structure cannot provide active side (unsaturated bond) for sulfur active center. The latter is due to macro-radical fragmentation, which decrease the polymer's molecular weight to a greater degree than radical combination increases it[1]. The β-scission of primary alkyl marco-radicals is identified to result in PIB degradation, as is illustrated in Scheme 1.1.



Scheme 1. 1 Radical-mediated degradation in polyisobutylene

Due to the low curability of polyisobutylene, isobutylene-isoprene copolymer, also called butyl rubber or IIR, was discovered in 1937. IIR is produced by solution cationic copolymerization of isobutylene and a small amount of isoprene in the presence of Friedel-Crafts catalyst ($AlCl_3$ or BF_3) at very low temperature (usually below -90°C). The isoprene units are distributed statistically randomly in the IIR chains and mostly in *trans*-1,4-positions.[2-4] The structure of IIR are illustrated in Figure 1.

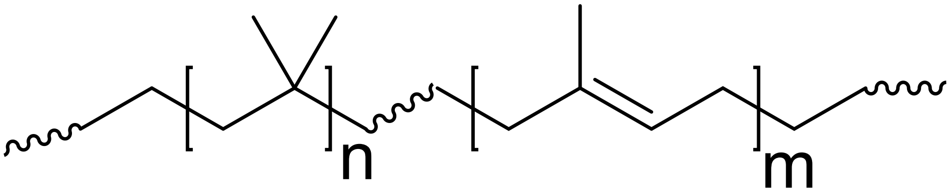


Figure 1. 1 Structure of isobutylene-isoprene copolymer (IIR)

The amount of isoprene units in macromolecule chains determined the lever of unsaturation of IIR. The present of isoprene units always severed as a chain transfer agent during the cationic copolymerization, which means when increasing the amount of isoprene units in macromolecule chains, it will decrease the molecular of overall polymer.[5] To balance the mechanical properties and the degree of unsaturation, the amount of isoprene in the commercial IIR types moves from 0.6 to 3 mol. %. The isoprene units in IIR chains have almost no influence on the properties of IIR. Thus, like the polyisobutylene (PIB), butyl rubber exhibits very good resistance to ozone and atmospheric condition and to chemical attack by acids, inorganic salts, and alkalis. At the same time, it has good elastic properties (glass transition temperature around -70°C), vibration damping abilities, and high coefficient of friction. The most valuable properties is that, butyl rubber have excellent impermeability to gases.[4, 6] These properties make the butyl rubber widely use in the production of bladders, inner liners, curing bags and diaphragms, steam hoses, shock absorbers, electrical insulators, and mechanical goods.[6-10]

1.2 Crosslink of elastomers

Uncross-linked elastomer exhibit viscoelastic behavior which means when you impose mechanical stress on an elastomer will result in relaxation, due to the large-scale mobility of polymer chains. In an amorphous, uncross-linked polymer that is above its glass transition temperature (Tg), the ability to resist deformation is directly proportional to the entanglements of the constituting polymeric chains.[11] But these entanglements or junctions will not always exist, so that the polymer cannot sustain the resistance of deformation. Such behavior limits the application of uncross-linked elastomers under prolonged period of stress. To overcome this disadvantage, different kinds of cross-linking process can be used to make a three-dimensional crosslinked network, which can hold the chain in place when subjected to prolonged period of stress.[1]

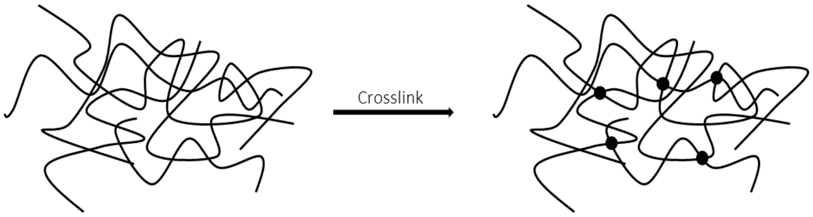


Figure 1. 2 Crosslinking of polymer chains

After crosslinking, the properties of elastomers significant changes at the molecular level. The long rubber molecules (molecular weight usually between 100,000 and 500,000 Daltons) become linked together with junctures (crosslinks) spaced along the polymeric chains, with the average distance between junctures corresponding to a molecular weight between crosslinks of about 4000 and 10,000 Daltons. Because of network formation, the rubber becomes essentially insoluble in any solvent, and an increase in the number of junctures or crosslinks in some cases can gives an increase in mechanical properties[12]

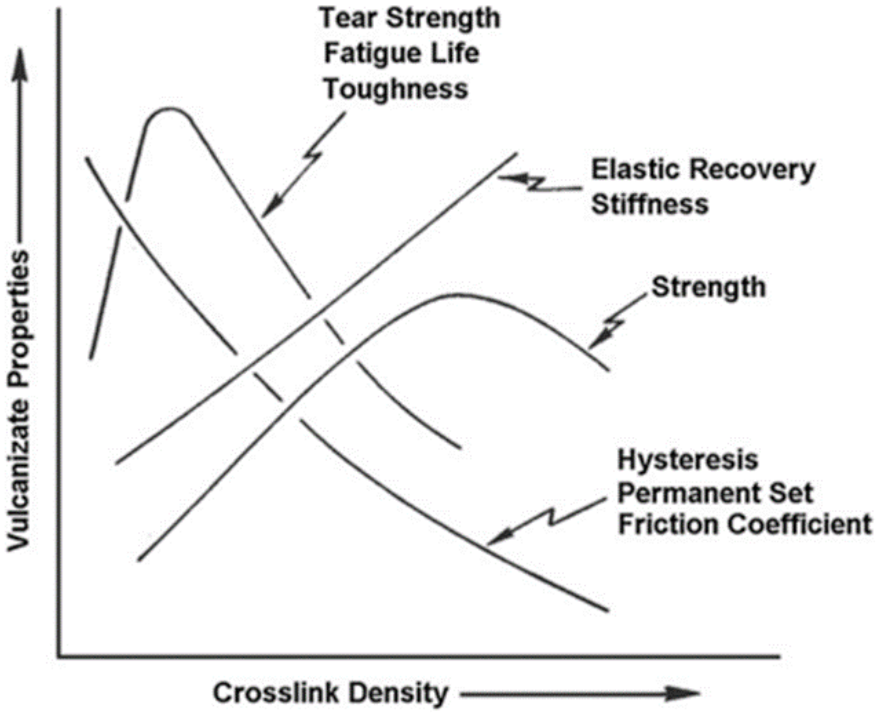


Figure 1. 3 Vulcanizate properties as a function of the extent of vulcanization[12]

1.3. Crosslink methods of isobutylene rich elastomers.

Polyisobutylene cannot be crosslinked via either sulfur system or peroxide system. However, when introducing isoprene units into the polymer chain, butyl rubber can be crosslinked via several methods. The curing systems suitable for crosslinking of IIR-based rubber compounds include traditional sulfur-accelerator system, phenol-formaldehyde resins, and quinones.[4, 12]

1.3.1 Sulfur crosslinked isobutylene rich elastomers

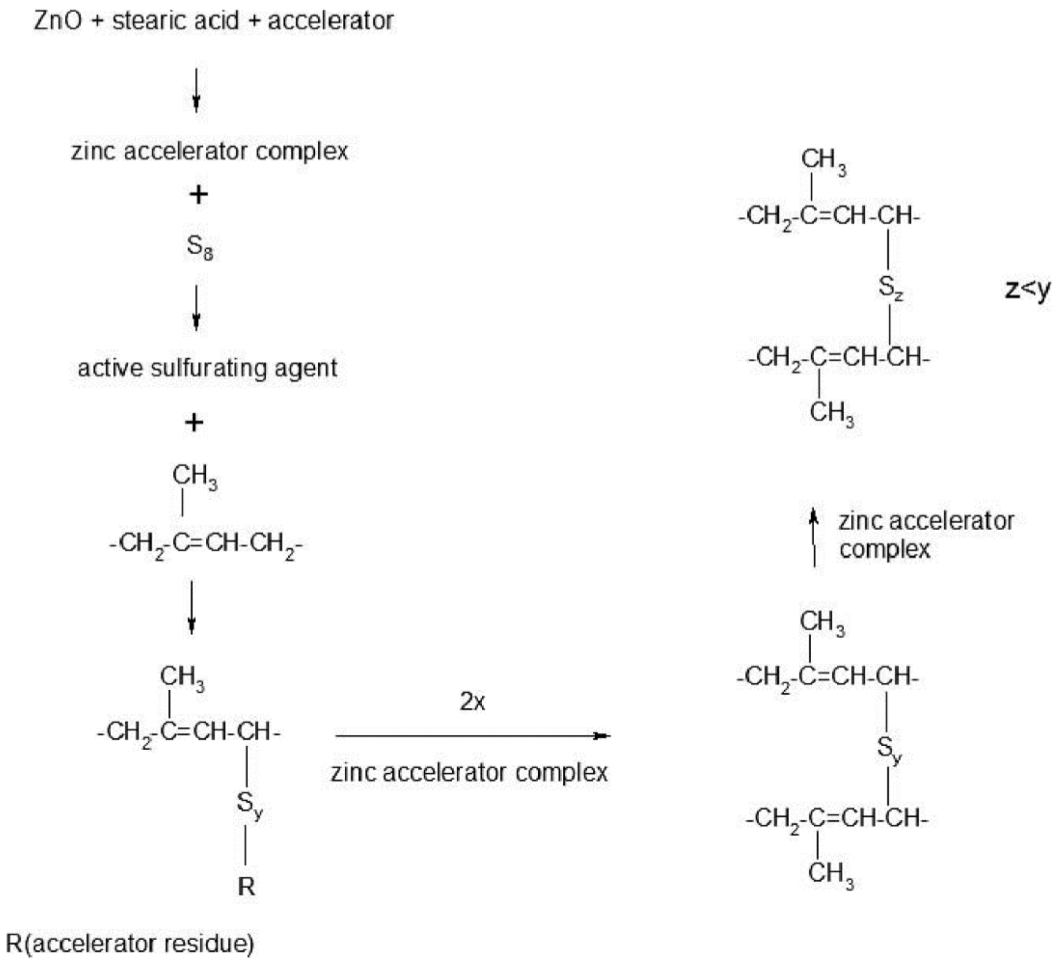
The first sulfur-curing method was discovered by Charles Goodyear in 1839.[13] His method, treating natural rubber with sulfur at high temperature, was first used in Springfield, Massachusetts. Tomas Hancock[14] used essentially the same process about a year later in England. The initial vulcanization process was accomplished by elemental sulfur, about 8 parts per 100 rubber (phr), and cost five hours at 140°C. The introducing of zinc oxide can reduce the reaction to three hours. But due to the slow curing rate and low vulcanization efficiency, unaccelerated sulfur vulcanization is no longer used for commercial goods.

In 1906, the accelerator-sulfur vulcanization system was discovered by Oenslager[15] who studied the effect of aniline in sulfur vulcanization. After that, guanidine, dithiocarbamates, mercaptobenzothiazole and benzothiazolesulfenamide were developed as accelerators[16]. The addiction of accelerator can drastically decrease vulcanization time, at the same time increase the sulfur efficiency.

Sulfur-accelerator system can be used in the crosslinking of almost all unsaturated elastomers, including butyl rubber. However, even if introducing isoprene units into the isobutylene polymer chain, the concentration of double bonds in IIR is about 30-50 times lower than that in NR, BR and SBR.[17] Vulcanization rate of IIR with systems similar to those applied for general-purpose rubbers would be very low. Therefore, a much efficiency vulcanization systems must be used for its vulcanization, and the vulcanization temperature must be higher.

Sulfur curing system with lower amount of sulfur and a higher amount of accelerator, thus called efficient (EV) or semi-efficient systems, are preferred for IIR vulcanization[18]. An adequate rate and degree of vulcanization can be achieved only by use of rapid effect accelerators. These include fast accelerators (thiazoles, sulfenamides), very fast accelerators (thiurams), ultra-accelerators (dithiocarbamates), and their combinations, or systems based on sulfur donors.

The sulfur crosslink of IIR proceeds via isoprene structural units with the formation of sulfidic cross-links, and the sulfidation is almost entirely led by the substitution of allylic hydrogen atoms, which was illustrated on Scheme 1.2[17, 19].



Scheme 1. 2 Sulfur crosslinking of IIR[17]

The sulfur-cured vulcanizates possess high values of tensile strength and tear strength; they also show good elastic and dynamic behavior, good abrasion resistance, and resistance to dynamic fatigue.[4, 20]

The main disadvantage of sulfur-cured IIR is low curing rate, which is determined by the low degree of double bonds in the macromolecule chains. Even with EV curing system, butyl rubber cannot match the vulcanization rate of other general-purposed rubbers. Even with the excellent gas impermeability, the unable to co-vulcanizate with other rubbers limits the usage of IIR in tire industry.

To deal with this disadvantage, halogenated butyl rubber was discovered. Halogenated butyl rubber was first studied by Morrissey and his coworkers at Goodrich in 1955. It was produced by chemical modification of IIR. Chlorination is used to produce CIIR, whereas bromination is used to generate BIIR. Figure 1.4 shows the most common forms of halogenated isoprene units in halogenated butyl rubber. Structure I, the predominant structure in halobutyl rubbers, represents 80–90%, followed by structure II, representing from 10 to 20%. The other forms of halogenated isoprene units can occur only rarely (< 2%).[21]

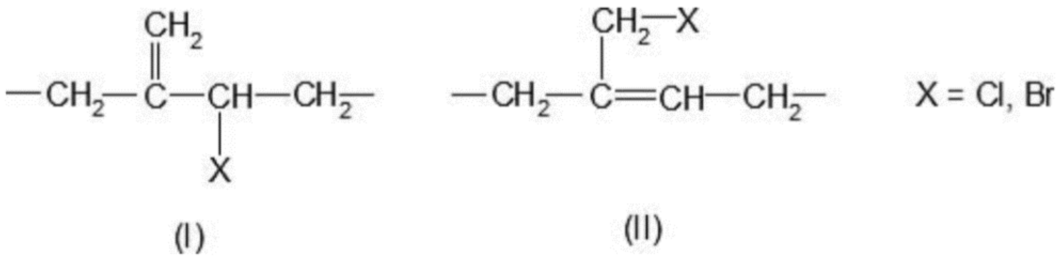


Figure 1. 4 Halogenated isoprene structural units in halogenated butyl rubbers.[4]

In principle, after the halogenation, the halogenated butyl rubber can be crosslinked with the same curatives of IIR, but the vulcanization proceeds faster and with a higher degree of crosslinking of the final vulcanizates.[4] The increase of reactivity can be attributed to the lower bond energy of carbon-halogen bonds. Table 1.1 shows the different bond energy of carbon-carbon and carbon-halogen.

Table 1.1 the bond energy and bond lengths of carbon and different atoms.[22]

Bond	Energy (J/mol)	Length (nm)
-C-C-	346	0.154
-C-H-	413	0.109
-C-F-	452	0.138
-C-Cl-	327	0.177
-C-Br-	209	0.194

The sulfur vulcanization of halogenated butyl rubber (usually BIIR) are used in tire inner liners where a high state of cure, fatigue resistance, tensile and tear strengths, and adhesion to general purpose rubbers in components adjacent to the inner liner are important. [23]

1.3.2 Phenol-Formaldehyde resin crosslinked isobutylene rich elastomers.

In 1951, Zapp and his coworkers studied the stoichiometry of sulfur vulcanization with IIR[24] and point out the long-term aging problems of sulfur cured butyl rubber.[25] Figure 1.5 points out the aging problems of sulfur cured butyl rubber when the temperature above 350°F.

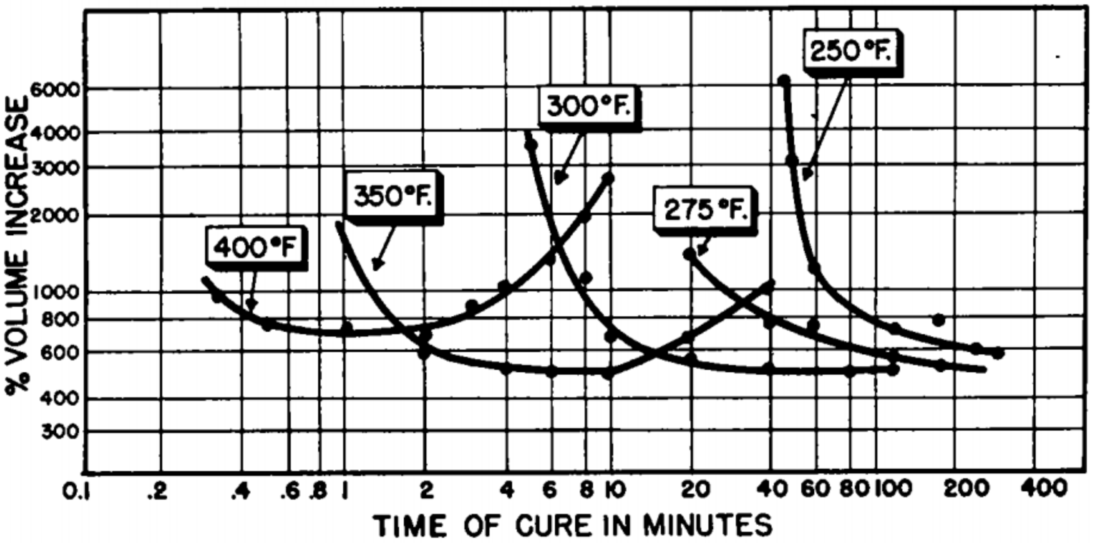


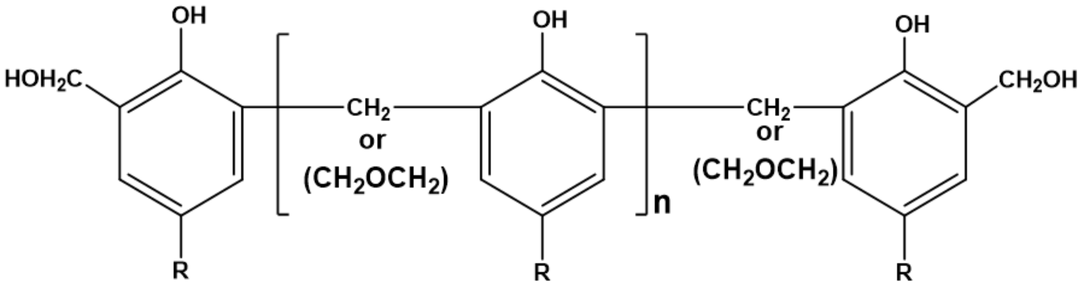
Figure 1. 5 Aging problems of sulfur cured IIR[25]

The low heat aging stability of sulfur vulcanized IIR limits the lifetime of curing bag and bladders. Table 1.2 gives the dissociation energy of different bonds in rubber crosslinks. The aging problems of sulfur cured butyl rubber mainly because the low bond energy of S-S bonds and C-S bonds compared with C-C bonds.[26]

Table 1.2 Dissociation energy of bonds in rubber crosslinks[26]

Bond type	**Dissociation energy, kcal/mole**
alkyl-C-C-alkyl	80
alkyl-C-S-C-alkyl	74
alkyl-C-S-S-C-alkyl	54
alkyl-C-Sn-Sm-C-alkyl	34

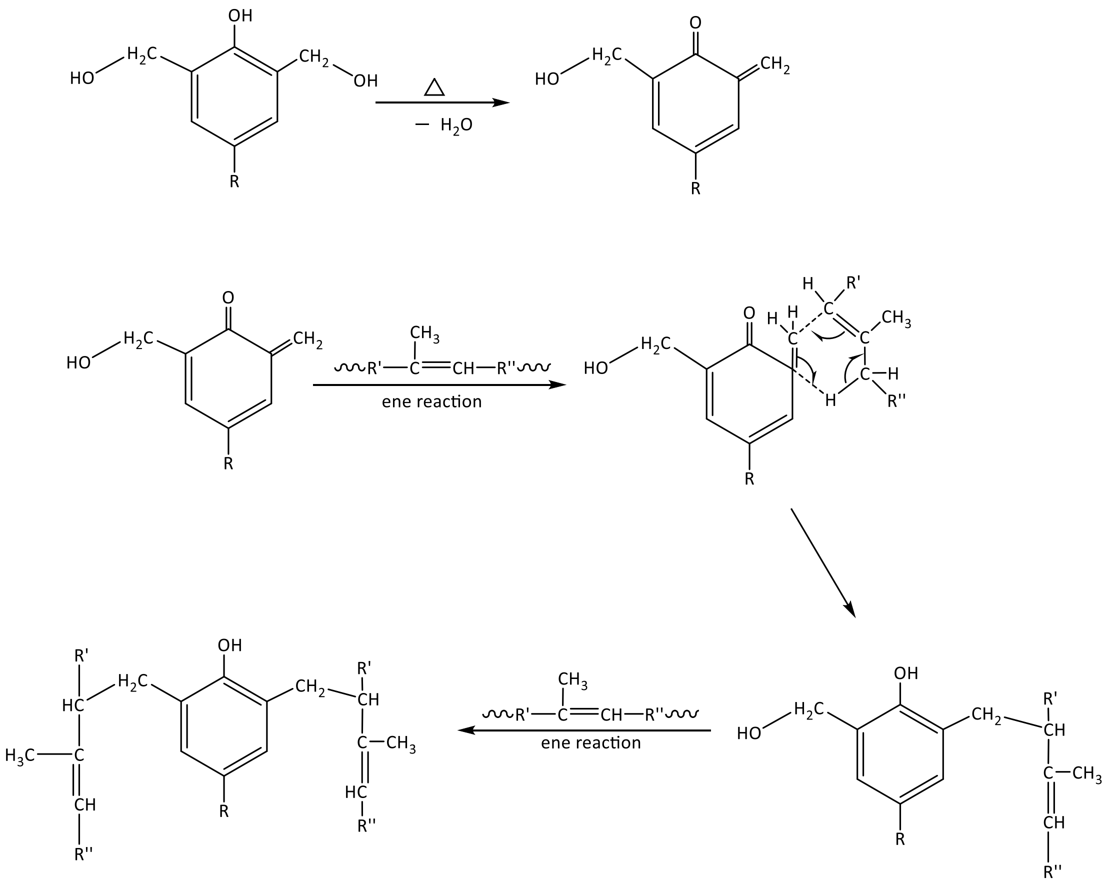
A major technical advancement for increasing the service life of curing bags was the development of phenol-formaldehyde resins for vulcanizing IIR.[27] Figure 1.6 shows the structure of general used resin for butyl rubber vulcanization.



R--- alkyl or hydrocarbyl group
n--- vary from 0 to 5-6

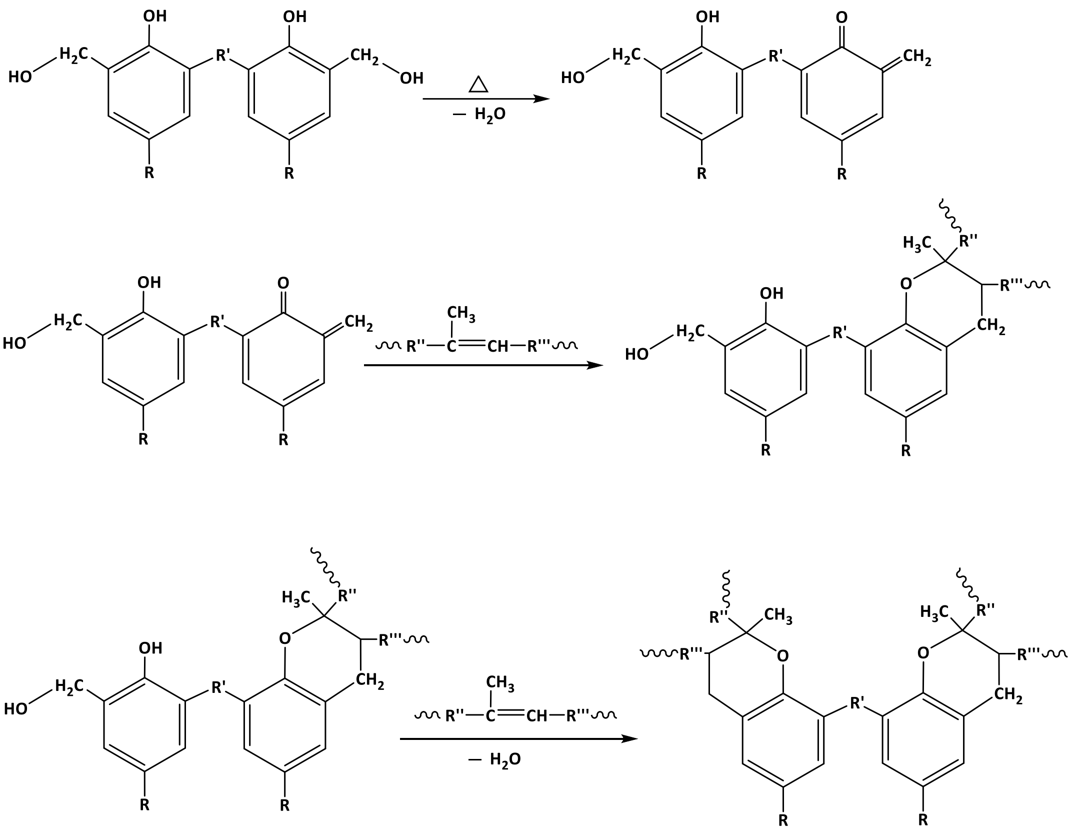
Figure 1. 6 Structure of general used phenol-formaldehyde crosslinker.

Resin-cured IIR exhibit good heat aging stability and good resistance to oxygen, ozone, and reversion.[28] The reaction mechanisms of resin cross-linking have been the subject of ongoing research. Two mechanisms have been proposed for resin curing of IIR. Van der meer reported a possible mechanism of phenol resin vulcanization[29] (shows in Scheme 1.3).



Scheme 1. 3 Van der meer's resin vulcanization mechanism[27]

Another alternating mechanism was reported in several papers (shows in Scheme 1.4 Chroman mechanism of resin vulcanization). Both Van der meer's mechanism and Chroman mechanism require the phenol resin lost water and form a quinone structure, and then this quinone structure can react with the double bond in the polymer chains. A Netherlands' scientist, Martin Van Duin[30] did some low-molecular weight model studies, it shows that both 'ene' reaction's product and cycloaddition (Diels-Alder addition) reaction's product will present in the curing process. With the increasing of temperature, the cycloaddition product will predominate, at the same time the 'ene' product will minimize[30]. Regardless the mechanism, the resin vulcanization can form a more stable carbon-carbon crosslink bond, which is more stable during long-term application than sulfur vulcanization.



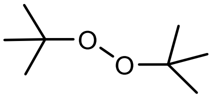
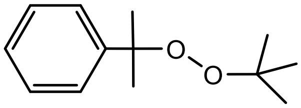
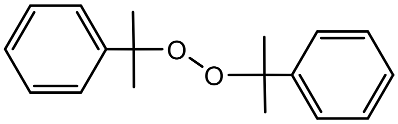
Scheme 1. 4 Chroman mechanism of the resin vulcanization[27]

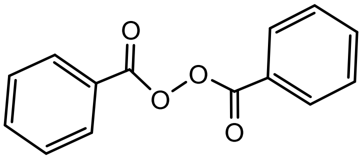
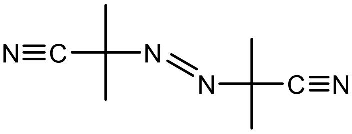
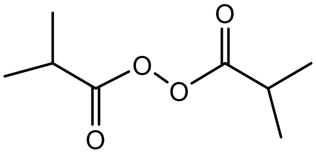
1.3.3 Peroxide crosslinking of isobutylene rich elastomers.

The peroxide cured system was first discovered by Ostromislenski in 1915[31] by using benzoyl peroxide to crosslink nature rubber (NR). After that, some scientists have been working on the peroxide vulcanization to figure out the principle of choosing different peroxide and the mechanism of the peroxide vulcanization. A common convention that is used to represent the stability of a peroxide is the *ten-hour half-life temperature*[32]. This is a definition as the temperature required to decompose a half of a peroxide sample in ten hours[32]. Table 1.3 shows *ten-hour half-life temperature* of different peroxides. The selection of a peroxide in a specific application usually involved a trade-off between the scorch time and process speed. Peroxide with low ten-hour half-life temperature has lower stability, which can lead to a short scorch time. On the other hand, peroxide with higher ten-hour half-life temperature requires a higher vulcanization temperature but it is unlikely to cause scorch.

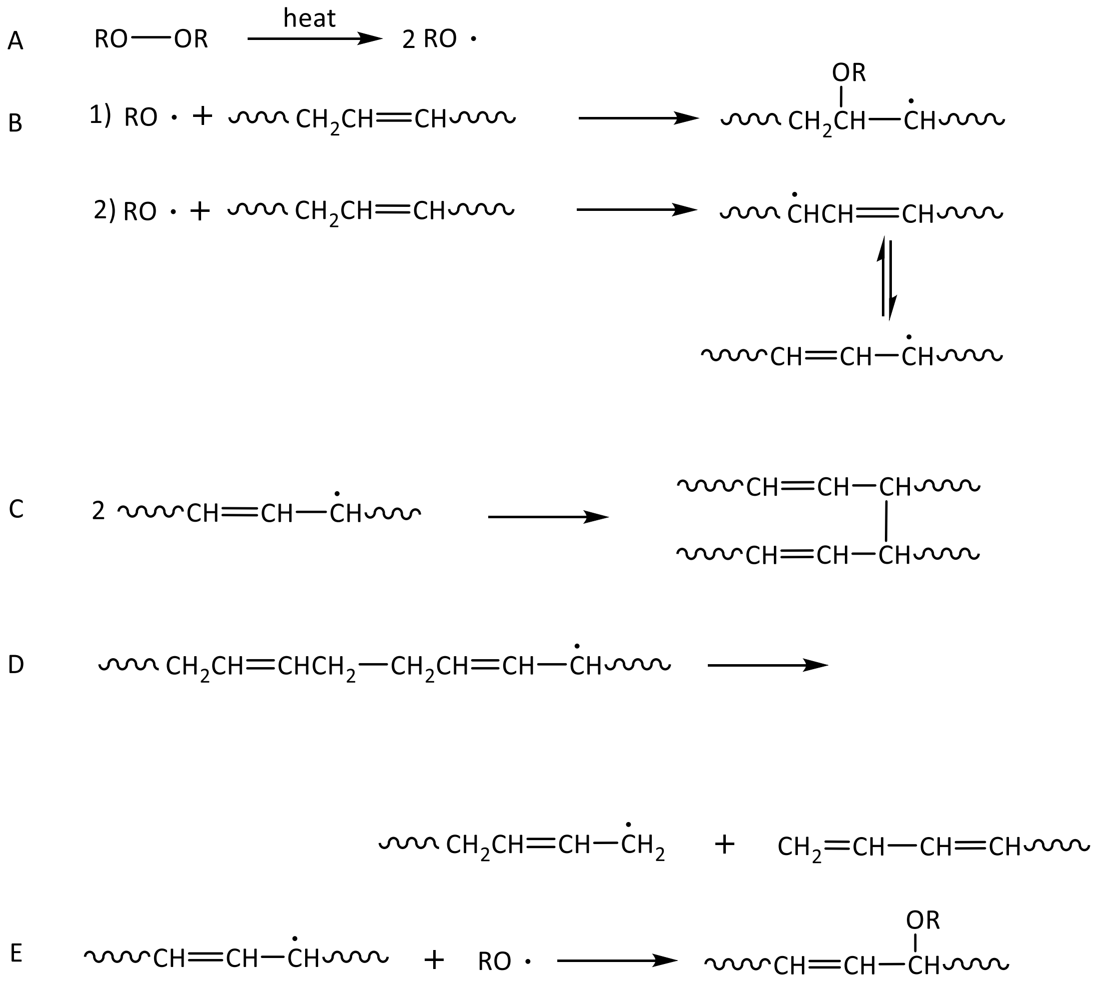
The driving force in peroxide vulcanization is the free radical. The mechanism of peroxide crosslink and crosslink efficiencies are studied by Thomas[33] and Loan[34]. The mechanism of peroxide crosslink is shown in Scheme 1.5.

Table 1.3 Ten-hour half-life temperature of different peroxides

Peroxide structure	**Temperature (°C)**
Di-*tert*-butyl peroxide 	123
***tert*-Butyl cumyl peroxide** 	117
Dicumyl peroxide 	114

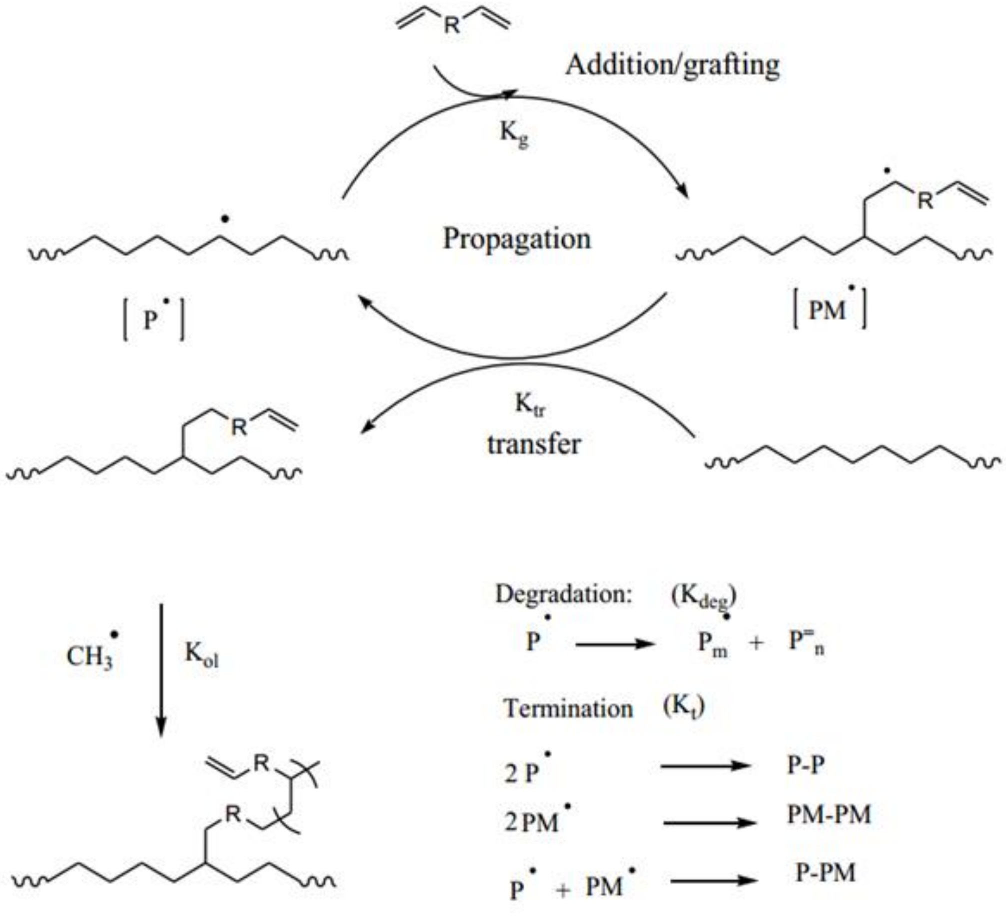
Benzoyl peroxide 	72
2,2’-Azodi(isobutyronitrile) 	63
Isobutyryl peroxide 	23

Then Fisher and Gray were further elucidated the peroxide curing mechanism[35]. They founded that the unsaturation of the rubber was not affected by the curing process. Then it was assumed that the crosslinking process didn’t depend on the unsaturation. It is an important advantage over sulfur vulcanization system, since sulfur was ineffective in vulcanizing fully saturated polymer such as EPM (ethylene-propylene copolymer).



Scheme 1. 5 Peroxide crosslinking mechanism[34]

However, the use of organic peroxide for crosslinking of IIR is undesirable, as pervious illustrated in Scheme 1.1 peroxide-derived radicals formed during the vulcanization step cause the chain scission of rubber chains instead of crosslinking. Even if, in nature, IIR cannot be crosslinked via peroxide, several attempts were made to make the IIR peroxide curable. In 1964, Loan tried to increase the amount of isoprene units in butyl rubber to make it peroxide curable. It shows that the chain scission efficiency falls very quickly as the unsaturation is increased[5]. Such effect can result if the radicals from the peroxide react with the isoprene units without having any chain scission reaction. But if we increase the isoprene units in the butyl rubber chains, it will result in a lower molecular polymer because the isoprene units are the chain transfer agent during the synthesis of polyisobutylene. It is hard to get a high molecular weight polymer with high isoprene units in the polymer backbone. Another approach for the peroxide curable butyl rubber is the introduce of coagent. Coagent is polyfunctional monomer that can be added into peroxide curing system to stabilize the peroxide thus can increase the extent of crosslinking[1]. Halimatuddahliana[36], Rajan[37] and Shanmugam used coagent-peroxide system to crosslink EPDM, NR and butyl rubber, respectively. Shanmugam introduced a concept named coagent assisted peroxide vulcanization (shows in Scheme 1.6).

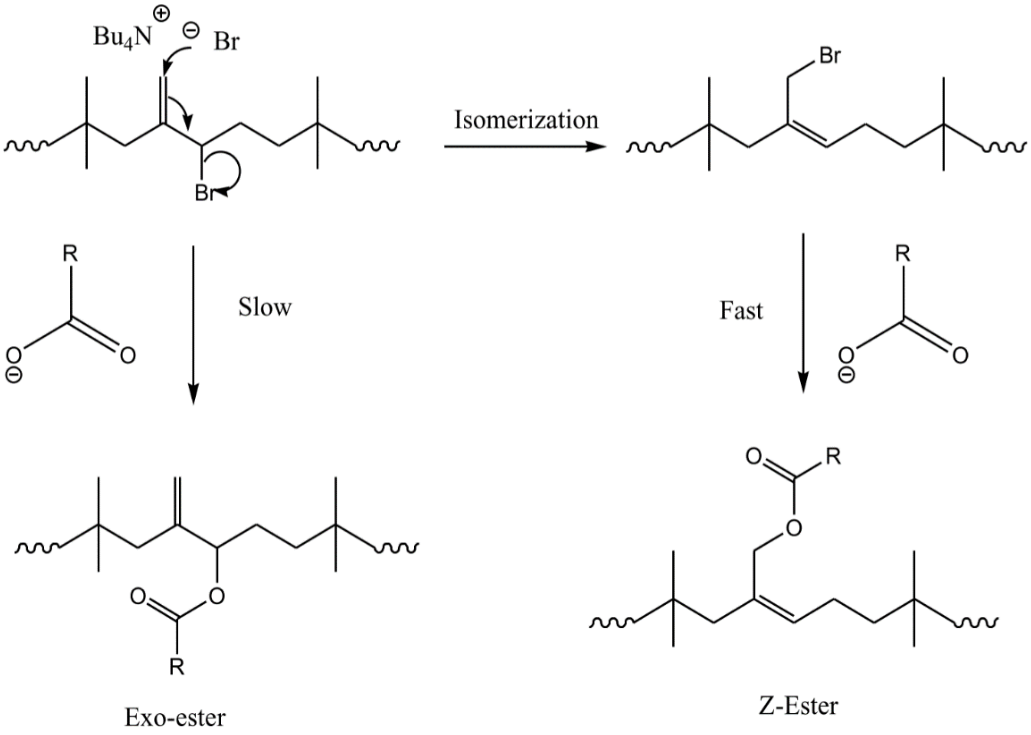


Scheme 1. 6 Coagent assisted peroxide vulcanization mechanism[1]

the coagent assisted peroxide vulcanization. When the grafting cycle is repeated, the crosslinking formed successfully without chain scission. The most widely considered side reaction is the homopolymerize of the coagent. Some people reported that it can be minimized by the ceiling temperature effect[1]. In most cases, the homopolymerize need to be considered.

1.4 Peroxide curable butyl rubber derivative

Many people are trying to prepare peroxide-curable butyl rubber, which could extend the application of butyl rubber.[38] Post-polymerization chemical modification is a useful approach to make peroxide curable IIR. It was derived from the production of halogenated butyl rubber, which owning a much higher reactivity site compared with regular butyl rubber. Ether, ester, ammonium or phosphonium functionalities are introduced into HIIR by nucleophilic substitution reaction, where aliphatic alcohol, carboxylate salt, amine or phosphine are used as nucleophile, depending upon the functionality to be introduced. These elastomer derivatives contain pendant polymerizable functional groups such as styrenic, acrylic, maleimidic and vinylic functional groups, which act as crosslinking sites. The network formed rapidly due to high reactivity of these functional groups. These systems, however, are is limited by the allylic bromide content of starting material (bromobutyl rubber), have issues with chain scission, and do not produce materials having mechanical properties comparable with sulfur cured butyl rubbers.[39-43] Scheme 1.7 illustrated one of the approaches of chemical modification in bromobutyl rubber.

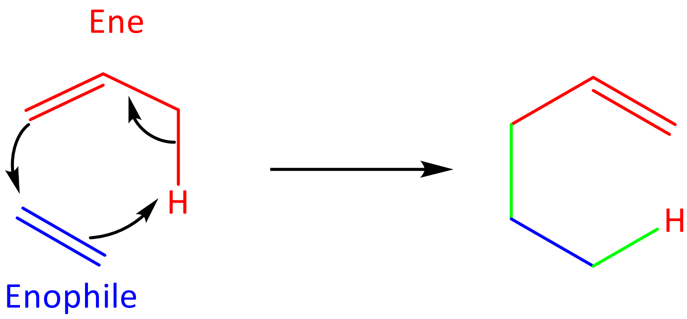


Scheme 1. 7 Ester modification of bromobutyl rubber[1]

Another peroxide-curable IIR is synthesized via Suzuki-Miyaura coupling reaction of HIIR with 4-vinylphenylboronic acid and phenylboronic acid, the crosslinking density of resulting polymer is controlled by changing ratio of two boronic acid. In this system, however, material has to be purified for synthesis, since the acidic residue contained in material spoils the catalyst, which results in the low coupling efficiency.[44] Similarly, the epoxidized butyl rubber was synthesized by using m-chloroperoxybenzoic acid with IIR. The ring-opening/elimination of epoxidized butyl rubber provides another way to prepare multifunctional graft copolymers, but does not produce materials having mechanical properties comparable with sulfur cured butyl rubbers.[45-47] In other cases, maleic anhydride has been grafted on IIR by using peroxide to improve its adhesion performance, but this approach was found to cause decrease of molecular weight of IIR.[48]

1.5 Previous work

Our previous work combined the chemical modification methods and coagent method. Using alder-ene reaction to chemical modification of IIR. Scheme 1.8 illustrated the mechanism of alder-ene reaction.



Scheme 1. 8 The mechanism of alder-ene reaction[49]

After the modification, with the assisted of coagent *N*,*N*′-(1,3 Phenylene)dimaleimide (DMI) (3-14 phr), IIR can be crosslinked under 0.1-0.5 phr of dicumyl peroxide (DCP) without chain scission. The mechanical properties including tensile strength, elongation and toughness are comparable or even better than sulfur cured butyl rubber. However, the coagent DMI, is highly toxic in contact with human skin and fatal if inhaled. With the consider of human health, a less toxicity coagent should be used for butyl rubber crosslinked.

CHAPTER II

EXPERIMENTAL

The experimental section is divided into three sections discussing materials, instrument and synthesis.

2.1 Materials

All materials were purchased from Sigma-Aldrich or Oakwood and used as received except ethyl propiolate, which were dried over Na/K, distilled, and stored under nitrogen. Exxon Butyl 268S, Bromobutyl rubber 2222 was donated by Goodyear company.

2.2 Instrument and Procedure

2.2.1 Nuclear Magnetic Resonance (NMR)

Chemical structures of products were characterized by a Varian Mercury 300-MHz or a Varian Avance 500 MHz nuclear magnetic resonance (NMR). 1H chemical shifts were determined using solvent peaks as the references. The solvent for NMR was Chloroform-D, Dimethyl sulfoxide-D6, Benzene-D6.

2.2.2 Gel Permeation Chromatography (GPC)

GPC was performed at 30 °C using a Tosoh HLC8320GPC with two TSK-GEL SuperH3000 columns and one TSKGEL SuperH5000 column equipped with a refractive index detector and THF as solvent. The flow rate was 0.350 mL/min. THF solutions of polymers (3 mg/mL) were prepared and filtered through 0.45 um nylon microfilters before injection. The molecular weight was determined relative to polystyrene standards.

2.2.3 Rubber Compounding and Curing Kinetics Test

The formulation of butyl rubber and its derivatives with peroxides and coagents was summarized in table below. The rubber compounds were mixed with a two-roll mill at 50°C. The result sample (5 g) was placed between two heated moving dies at 110 °C. Sinusoidal shear was applied with frequency of 1.66 Hz and deformation angle of 0.5°. Torque of the tested sample was measured during the test period; Torque vs time plot was drawn to studying the curing kinetics of different formulation.

2.2.3.1 Compounding of IIR (Polymer 1) with curatives by using a two-roll mill

The recipe for compound **1a** is given in Table 2.1. While IIR was passed through the two-roll mill at 50 ℃. Sulfur, stearic acid, zinc oxide and tetramethylthiuram disulfide (TMTD), mercaptobenzothiazole (MBT) were added to the rubber slowly. The compound **1a** was sheet out from two-roll mill after 30 times pass. The result compound was placed on a Dake Hydraulic Mold 4419 hot press and vulcanized at 160 ℃. The curing time is t_{90} + 10 min.

The recipe for compound **1b** is given in Table 2.2. While IIR was passed through the two-roll mill at 50 ℃. Benzoyl peroxide (BPO) and trimethylolpropane trimethacrylate (TMPTMA) were added to the rubber slowly. Each compound was sheet out from two-roll after 30 times pass. The result compound was placed on a Dake Hydraulic Mold 4419 hot press and vulcanized at 110 ℃. The curing time is t_{90} + 10 min.

Table 2. 1 Recipe for compound **1a**.

Compound	Polymer 1	Sulfur	TMTD	MBT	ZnO	Steric Acid
1a	100 g	2 g	1 g	0.5 g	5 g	1 g

Table 2. 2 Recipes for compounds **1b**.

Compound	Polymer 1	BPO	TMPTMA
1b	100 g	2 g	10 g

2.2.3.2 Compounding of Et-g-IIR (Polymer 2) with curatives by using a two-roll mill

The recipe for compound **2a-2i** is given in Table 2.3. While IIR was passed through the two-roll mill at 50 ℃. Benzoyl peroxide (BPO) and trimethylolpropane trimethacrylate (TMPTMA) were added to the rubber slowly. Each compound was sheet out from two-roll after 30 times pass. The result compound was placed on a Dake Hydraulic Mold 4419 hot press and vulcanized at 110 ℃. The curing time is t_{90} + 10 min.

Table 2. 3 Recipes for compounds **2a-2i**.

Compound	Polymer 1	BPO	TMPTMA
2a	100 g	1 g	5 g
2b	100 g	1 g	10 g
2c	100 g	1 g	15 g
2d	100 g	2 g	5 g
2e	100 g	2 g	10 g
2f	100 g	2 g	15 g
2g	100 g	3 g	5 g
2h	100 g	3 g	10 g
2i	100 g	3 g	15 g

2.2.3.3 Compounding of Bromo-butyl rubber (Polymer 3) with curatives by using a two-roll mill

The recipe for compound **3a** is given in Table 2.4. While IIR was passed through the two-roll mill at 50 ℃. Benzoyl peroxide (BPO) and trimethylolpropane trimethacrylate (TMPTMA) were added to the rubber slowly. Each compound was sheet out from two-roll after 30 times pass. The result compound was placed on a Dake Hydraulic Mold 4419 hot press and vulcanized at 110 ℃. The curing time is t_{90} + 10 min.

Table 2. 4 Recipes for compounds **1b**.

Compound	Polymer 1	BPO	TMPTMA
3a	100 g	2 g	10 g

2.2.4 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was performed on an TA Q800 Dynamic Mechanical Analyzer. A compression-molded sheet was cut into strips of 20 mm × 10 mm × 1 mm. The initial clamp distance was set at 10 mm. In the stress-relaxation test, the test temperature was set as 25°C and kept during the whole test period. The sample was kept at 10% strained condition for 24 hours. Force, stress and modulus were measured during the test.

2.2.5 Tensile Test

Tensile tests were performed on an Instron Model 5567 equipped with a 1000 N load cell. The samples were cut into pieces with an ASTM D638 type V dumbbell die. Samples were held in two clamps with a 50 mm gap. Two extensometers were held with a 20 mm gap. The samples were extended at a rate of 500 mm/min at room temperature until failure.

2.2.6 Sol-gel and Swelling Test

Sample was weighed and put into a 20 mL vial. Then 15 mL hexane was added into vial to swell sample. Solvent was changed every 3 days. The total time for swelling sample was 1 week. To weigh swollen sample, solvent on the surface of sample was removed by Kimwipes and swollen sample was weighed quickly. Then sample was put back into vial to reach equilibrium state. The process was repeated 5 times to get average weight of swollen sample. After that, the swollen sample was put into tetrahydrofuran for

1 week to remove residual unreacted coagent TMPTMA, then transferred into vacuum oven until weight of sample did not change. The final weight is called the weight of dry sample. The gel fraction is defined as:

$$W_{Gel} = \frac{W_{dry}}{W_o} \times 100\% \qquad Eq_1$$

W_{Gel} is gel fraction

W_{dry} is the weight of dry sample

W_o is the weight of original sample

The crosslinking density was calculated by the Flory-Rehner equation[50-51]:

$$\text{In } (1-\varphi_r) + \varphi_r + \chi\varphi_r^2 = -\rho_{cx} V_s(\varphi_r^{1/3} - \frac{2\varphi_r}{f}) \qquad Eq_2$$

φ_r is volume fraction of rubber

χ is polymer-solvent interaction parameter, 0.516 is used here

V_s is molar volume of solvent, 130.8 cm^3/mol

f is functionality of crosslinks, 4 is used here.

ρ_{cx} is crosslinking density in compound, mol/cm^3

2.3 Synthesis

2.3.1 Synthesis of ethyl propiolate graft butyl rubber

IIR (1 in Scheme 1, Mw = 424858 g/mol, PDI = 2.720, 150 g, 40.2 mmol C=C) was first dissolved in 1500 mL anhydrous hexane under nitrogen atmosphere. Then ethyl propiolate (10 mL, 98.7 mmol) was added dropwise into flask and dissolved quickly. After completed addition, the mixture was stirred for ten minutes under room temperature. Then 1M stock solution of $EtAlCl_2$ in hexane (86 mL, 86 mmol) was transferred into the solution. The result solution was stirred for ten minutes under room temperature, then the flask was putted into a 50 °C water bath and reacted for 16 hours. Then the result solution was precipitated in ethanol stirred with mechanical stirrer. The solvent in rubber was removed under reduced pressure. The yield was 99%. Mw of polymer 2 was 390689g/mol, PDI = 3.861. The 1H-NMR spectrum of polymer 2 is shown in Figure 2.1. ^{1}H NMR (CHLOROFORM-d ,500MHz): d = 6.74 - 6.83 (m, 1 H), 5.73 - 5.80 (m, 1 H), 4.87 - 5.00 (m, 2 H), 4.15 - 4.22 (m, 2 H), 2.59 - 2.70 (m, 1 H), 1.94 - 2.02 ppm (m, 2 H)

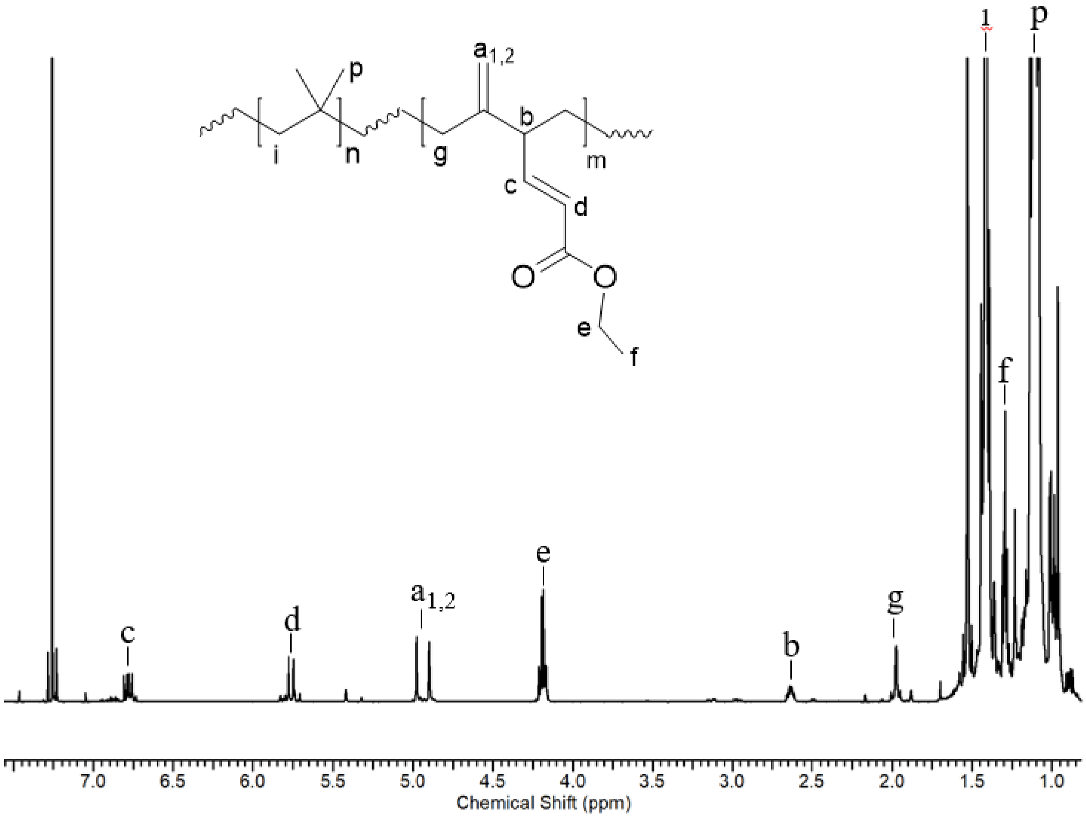
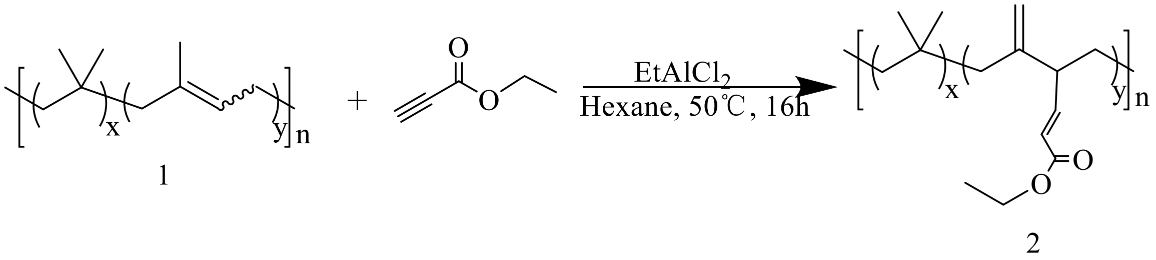


Figure 2. 1 ^{1}H spectrum of polymer **2** in $CDCl_3$.

The synthetic route is shown in Scheme 2.1.



Scheme 2. 1 Synthesis route of ethyl propiolate-g-butyl rubber (Polymer **2**)

2.3.2 Synthesis of ethyl propiolate grafted 2-methyl-2-butene

2-methyl-2-butene (Mw = 70.13 g/mol, 10 mL, 94.4 mmol) was first dissolved in 50 mL anhydrous hexane under nitrogen atmosphere. Ethyl propiolate (Mw = 98.1 g/mol, 2.44 mL, 24.1 mmol) was added dropwise into flask and dissolved quickly. The 1M stock solution of $EtAlCl_2$ in hexane (16 mL, 16 mmol) was added into the solution. The solution was stirred for 10 min, then the flask was transferred in 50 ℃ water bath. The reaction time was 10 hours; then 20 mL water was added into flask to stop the reaction. The result suspension was centrifuged to form two layers. The top layer was transferred in flask and pumped down to remove the solvent. The yield was 53%. The ^1H NMR spectrum of ethyl propiolate graft 2-methyl-2-butene is shown in Figure 2.2. ^1H NMR (CHLOROFORM-d ,500MHz): d = 6.91 (dd, *J*=15.7, 7.2 Hz, 1 H), 5.81 (dd, *J*=15.7, 1.3 Hz, 1 H), 4.76 - 4.83 (m, 2 H), 4.18 (q, *J*=7.0 Hz, 2 H), 2.97 (t, *J*=7.0 Hz, 1 H), 1.70 (s, 3 H), 1.29 (t, *J*=7.2 Hz, 3 H), 1.18 ppm (d, *J*=7.0 Hz, 3 H).

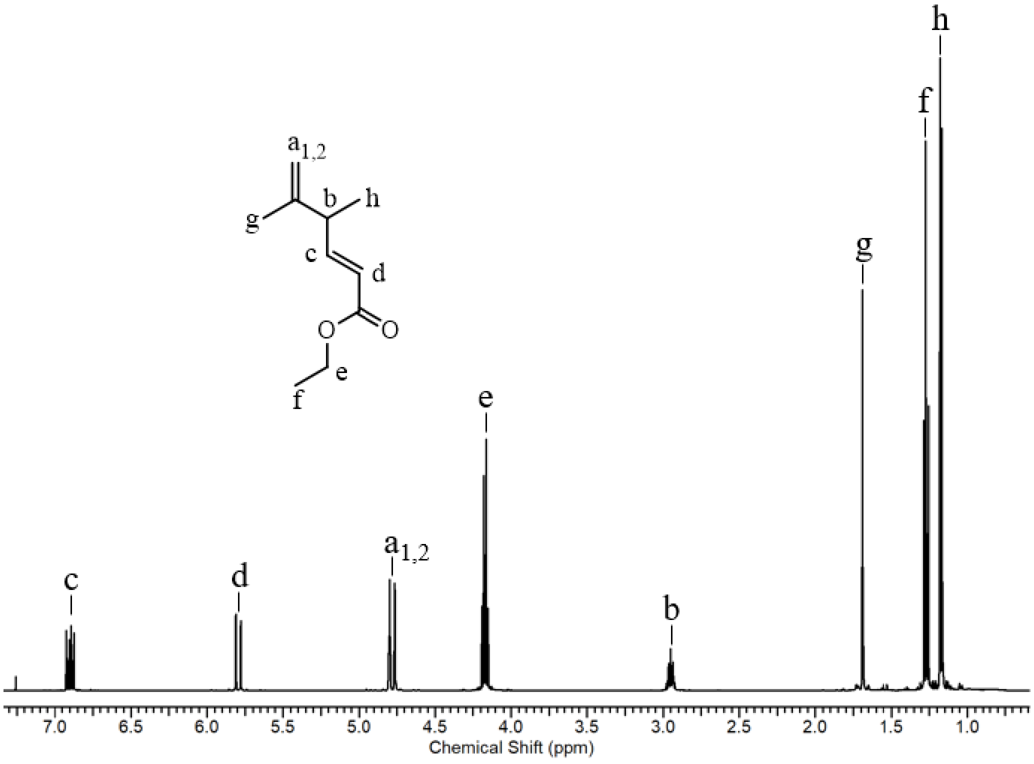
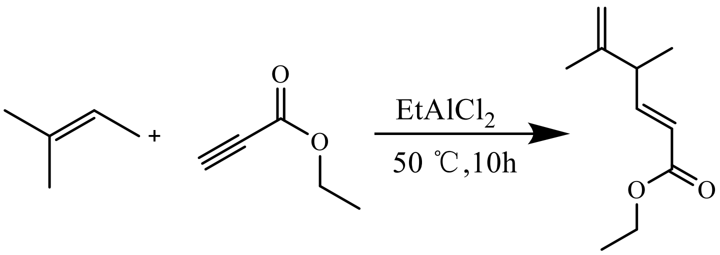


Figure 2. 2 ^1H spectrum of ethyl propiolate-g-2-methyl-2-butyene in $CDCl_3$.

The synthetic route is showed in Scheme 2.2 blow.



Scheme 2. 2 Synthesis route of ethyl propiolate-g-2-methyl-2-butylene

CHAPTER III

RESULT AND DISSCUSSION

3.1 Cross-linking kinetics of isobutylene-isoprene rubber (IIR).

The curing kinetics plot of butyl rubber (IIR) was measured via moving die rheometer (MDR) and was shown in Figure 3.1. Some important curing characteristics were summarized in Table 3.1. Figure 3.1 shows that the sulfur vulcanization of butyl rubber is relatively slow compared with peroxide crosslinking. However, the equilibrium torque of sulfur cured butyl rubber is two times higher than peroxide cured butyl rubber. That’s because during the peroxide crosslinking process, peroxide induced chain scission happened (Scheme 1.1), which drastically decreased the molecular weight of polymer and thus lower the equilibrium stage. The following sol-gel and swelling test would confirm that and indicated that even with the assistance of coagent TMPTMA, peroxide cannot be used as a crosslinker of unmodified butyl rubber.

Table 3. 1 Summary of curing characteristics of compounds **1a** and **1b**

Compound	**t_{10} (min)**	**t_{90} (min)**	**M_L (dNm)**	**M_H (dNm)**	**ΔM (M_H-M_L) (dNm)**
1a	4.57	22.98	1.25	5.35	4.10
1b	1.31	10.34	1.19	1.77	0.58

M_H maximum torque M_L minimum torque

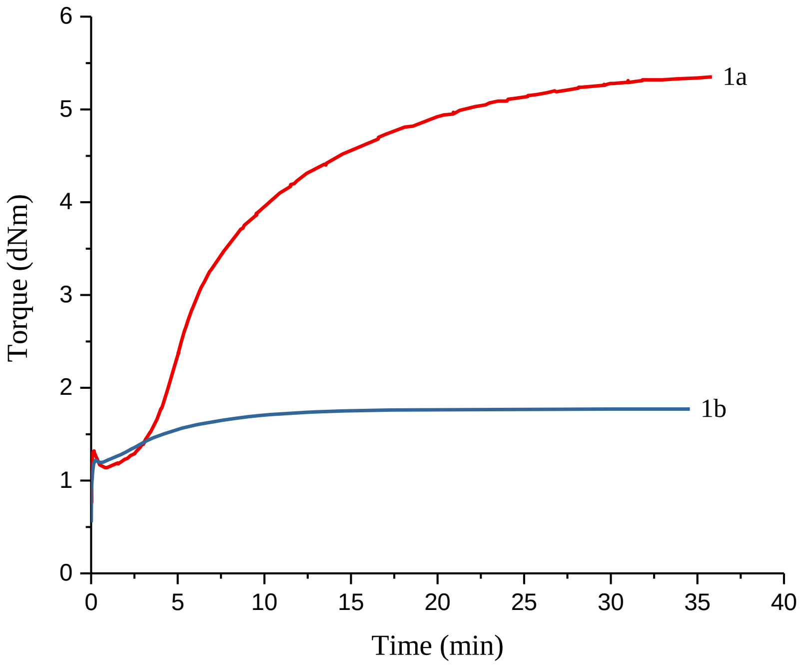


Figure 3. 1 Curing kinetic curves of butyl rubber

3.2 Cross-linking kinetics of butyl rubber derivatives.

The curing kinetics plot of ethyl propiolate grafted butyl rubber and bromo-butyl rubber were measured via moving die rheometer (MDR) and were shown in Figure 3.2. Some important curing characteristics were summarized in Table 3.2.

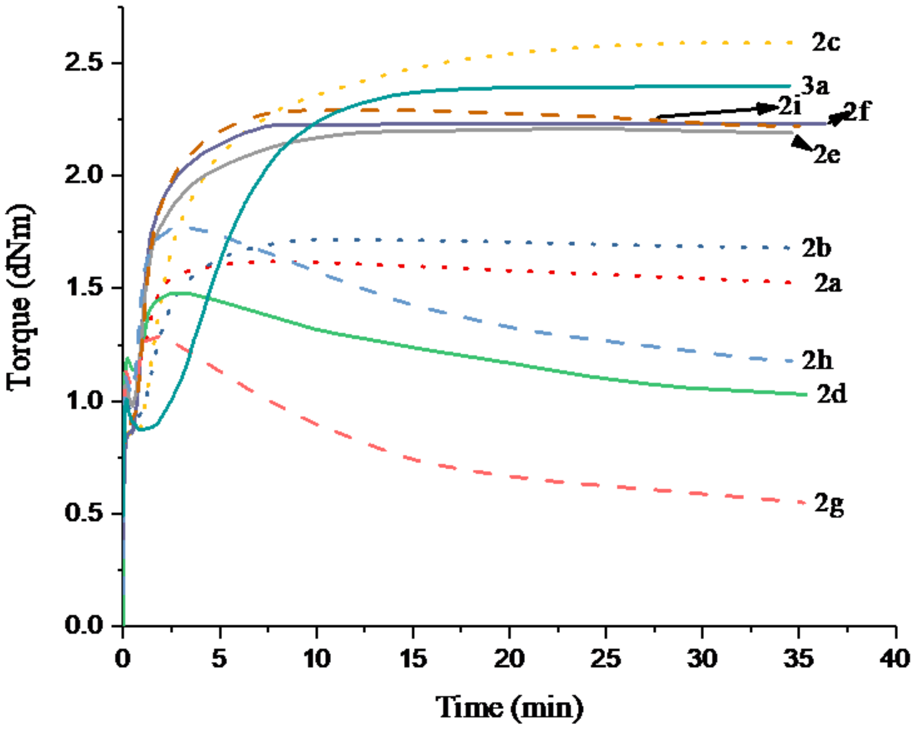


Figure 3. 2 Curing kinetic curves of Et-g-IIR and Bromo-butyl rubber

During the crosslink process, two compete reaction: crosslink and chain scission happened, in Figure 3.2, **2h**, **2d**, **2g** indicated that the chain scission reaction dominated the overall crosslink process. That chain scission reaction can destroy the equilibrium stage when the initial peroxide exhausted. The decreasing torque after reaching maximum torque can confirm that theory. That because the initial peroxide can H-abstraction of both allylic C-H bonds and primary C-H bonds. The allylic C-H radicals can form crosslinking bonds with another radical, while the primary C-H radicals only cause chain scission. After the deplete of initial peroxide, the only kind of radical left is primary C-H radical, which will further rearrangement into a double bond end group and another primary C-H radical. Also, from the Figure 3.2, **2a-2c**, **2d-2f**, **2g-2i**, when increasing the load of coagent TMPTMA, the chain scission reaction can be suppressed. According to the Figure 3.2, when loading with 15 phr TMPTMA, both **2c**, **2f**, **2i** (1 phr, 2 phr, 3 phr BPO) does not have chain scission. However, when loading with 10 phr TMPTMA, **2b**, **2e** does not have chain scission. When loading with 10 phr TMPTMA, only **2a** does not have chain scission. That indicates that adding more coagent such as TMPTMA can help suppressed the chain scission and thus makes the modified butyl rubber peroxide curable. However, since the coagent TMPTMA is immiscible with butyl rubber, the upper limit loading of TMPTMA is 15 phr, above the upper limit, TMPTMA could bloom from butyl rubber during the mill process.

Within the upper limit, **2c**, **2e**, **2f**, **2i**, and **3a** were sufficient to generate stable crosslink stage. The mechanical properties of those compounds would be discussed later.

Table 3. 2 Summary of curing characteristics of compounds **2a-2i** and **3a**.

Compound	**t_{10} (min)**	**t_{90} (min)**	**M_L (dNm)**	**M_H (dNm)**	**ΔM (M_H-M_L) (dNm)**
2a	1.16	1.96	1.16	1.63	0.47
2b	1.17	5.62	0.92	1.73	0.81
2c	1.17	13.37	0.83	2.62	1.79
2d	0.49	1.12	0.92	1.45	0.53
2e	0.75	6.36	0.98	2.21	1.23
2f	0.70	3.98	0.86	2.22	1.36
2g	0.04	1.15	0.54	1.29	0.75
2h	0.08	1.55	0.98	1.77	0.79
2i	0.76	4.52	0.90	2.30	1.40
3a	2.62	10.34	0.86	2.40	1.54

M_H maximum torque M_L minimum torque

3.3. Sol-gel and swelling test

The gel fraction and crosslinking density of compounds **1a-1b**, **2a-2i**, **3a** were measured by swelling test. The weight average molecular weight (Mw) of sol part in all these compounds were tested by GPC. The results were summarized in Table 3.3. According to the table 3.3, unmodified butyl rubber (1b) cannot be crosslinked by peroxide and coagent TMPTMA. After the modification, with proper ratio of peroxide/coagent, the Et-g-butyl rubber can be crosslinked by peroxide and generate sufficient enough degree of crosslinking. Compounds 2c, 2e, 2f, 2i can formed whole net-working after the crosslinking process. The low gel fraction of compounds 2a, 2b, 2d, 2g, 2h were caused by the chain scission reaction. With the addition of more coagent TMPTMA, both the crosslink density and gel fraction would increase. Compound 2i has the highest gel fraction, followed by 2c and 2e, which large amount of TMPTMA were added.

The crosslinking density of compounds in Table 3.3 is reciprocal to the molecular weight of sol part in compounds. It is probably because shorter polymer chains are not involved into the network when compound has higher crosslinking density. The crosslinking in compound comes from combination of two macroradicals in different polymer chains or macroradical is added on another polymer chain. Not all radicals form crosslinking. Radical could abstract hydrogen from isobutylene units to undergo chain scission. Or the radical would H-abstract the hydrogen in coagent and thus initiate the homopolymerized of coagent. It is apparently that coagent TMPTMA would homopolymerized when introduced with peroxide. So, it is necessary to introduce peroxide efficiency, which is defined as crosslinking density divided by moles of peroxide used per unit volume of compound. The formula is shown in equation 3. For compounds 2a-2i, with the same load of TMPTMA, the peroxide efficient was first increased and then decreased. While, with the same load of BPO, the peroxide efficient was increased with the loading of TMPTMA. It is because with the increasing TMPTMA loading, chain scission is mitigated, meanwhile there were more crosslinking forms between coagent TMPTMA and butyl rubber, which increases peroxide efficiency.

$$E_{cx} = \frac{\rho_{cx}}{n_{DCP}} \times \left(\frac{m_r}{\rho_r} + \frac{m_{DMI}}{\rho_{DMI}}\right) \qquad Eq3$$

E_{cx} is peroxide efficiency

ρ_{cx} is crosslinking density measured by equation 2, mol/m^3

n_{DCP} is the moles of DCP used in compound, umol

m_r is the mass of rubber in compound, g

ρ_r is density of rubber, 0.92g/cm^3

m_{DMI} is the mass of DMI in compound, g

ρ_{DMI} is density of DMI, 1.567g/cm

Table 3. 3 Gel fraction and crosslinking density of compounds **1a-1b, 2a-2i, 3a**

Compounds	**Gel Fraction (%)**	**Crosslinking Density (mol/m^3)**	**Mw of sol part (g/mol)**	**Peroxide Efficiency**
1a	90% ± 0.2%	112.5±4.3	10977	N
1b	48% ± 3.0%	0.8±0.5	1611095	0.01
2a	60% ± 1.4%	4.40 ±0.5	212909	0.12
2b	66% ± 1.7%	3.30 ±0.6	282728	0.09
2c	80% ± 1.7%	23.5±0.5	39132	0.69

2d	54% ± 2.0%	0.60±0.2	1524391	0.01
2e	79% ± 0.5%	20.6±4.4	46152	0.29
2f	77% ± 0.1%	67.0±6.2	13815	0.99
2g	47% ± 2.3%	0.20±0.1	4527633	0.01
2h	67% ± 2.6%	5.30±1.2	178140	0.05
2i	81% ± 0.3%	28.5±2.0	32412	0.28
3a	83% ± 0.6%	26.9±0.3	34190	0.38

3.4 Mechanical properties of different compounds

The key parameters of compounds 1a-1b, 2a-2i, and 3a were summarized in Table 3.4. Stress-strain curves of compounds 1a-1b, 2a-2i, and 3a were shown in Figure 3.3.

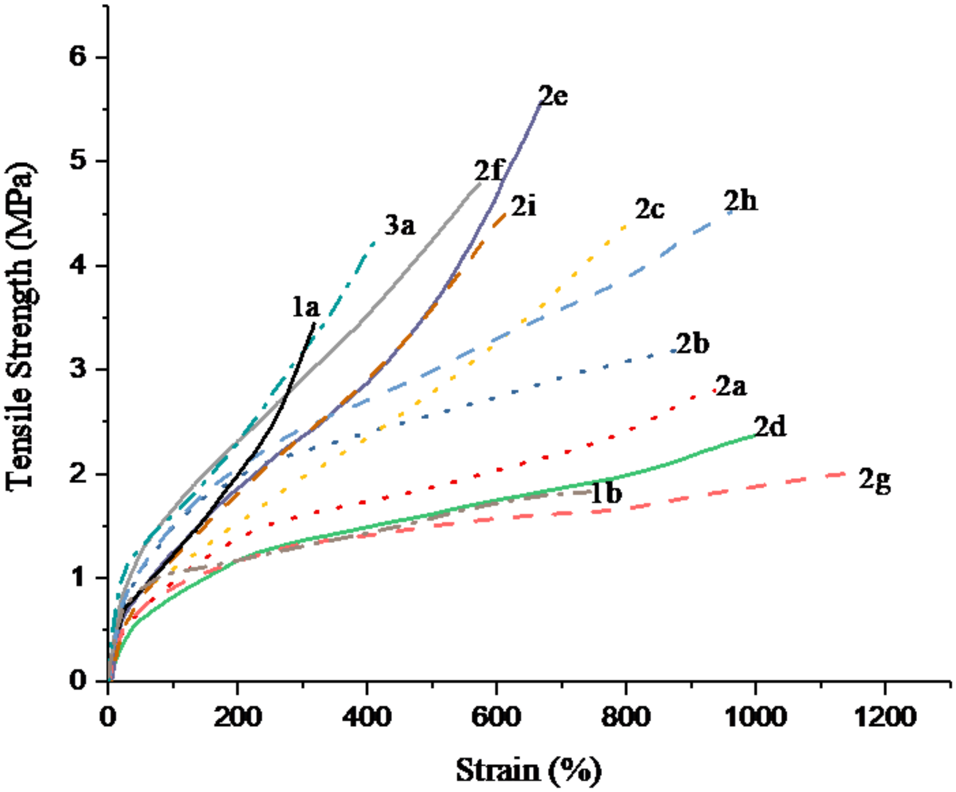


Figure 3. 3 Stress-strain curves of compounds 1a, 1b, 2a-2i, and 3a

Compound 1a is crosslinked by sulfur, which has high tensile strength and moderate elongation without chain scission. The formulation were reported in our group's previous publication[52], which can be considered as a standard reference when comparing some mechanical properties with the new crosslinked butyl rubber. Compound 3a is crosslinked via a similar formulation (2 phr BPO and 10 phr TMPTM) with the new butyl rubber and can be considered as a Bromo-butyl rubber reference. Base on the mechanical properties of 2a-2i, 1a-1b, and 3a and the load of coagent TMPTMA and BPO in previous Table 2.1- Table 2.4. The mechanical properties such as tensile strength and elongation of compound 2c, 2e, 2f, 2i are better than the standard sulfur cured butyl rubber 1a, and even better than peroxide cured bromo-butyl rubber 3a.

Our previous works using coagent DMI and DCP to crosslink the same Et-g-Butyl rubber, the best mechanical properties is 4.0 MPa with 350 % elongation. The crosslink density is around 40-100 mol/m^3, and the gel fraction is around 89%. Both the crosslink density and mechanical properties of our previous work is comparable with sulfur standard. However, when introducing TMPTMA as a coagent, the crosslink density and gel fraction is much lower than sulfur standard and our previous DMI coagent. According to Figure 3.3, compound 2e has the greatest mechanical properties, which has the highest tensile strength and moderate elongation. Using compound 2e as an example, according to the Table 3.3 and Table 3.4, both the gel fraction and crosslink density of compound 2e is much lower than that of sulfur stand and our previous DMI coagent. However, compound 2e has 37% higher tensile strength than sulfur stand and our previous sample, at the same time it can undergo almost 100% longer elongation.

The reason why compound 2e has both high elongation and high tensile strength is still not clear. A careful crosslink mechanism study is required for that, however, since the limit schedule, it will not include in this thesis. A main explanation of this phenomena is that during the crosslinking process, three compete reaction happened: a) crosslinking reaction b) chain scission reaction c) homo-polymerization of coagent. Both the reaction b and c can deteriorate the overall crosslink density. Coagent can serve as a macro-radical scavenger (Scheme 1.6), which can stable the macro-radical to suppress the chain scission reaction. Coagent DMI is a typical of this, the structure of DMI (N,N′-(1,3-Phenylene)dimaleimide) is hard to homo-polymerize, so that eliminate a potential waste of peroxide at the same time can increase the crosslink density due to the lack of compete reaction. However, unlike the coagent DMI, the coagent: trimethylolpropane trimethacrylate (TMPTMA) is an acrylate type of coagent. That means during the crosslink process, the homo-polymerization of TMPTMA is unavoidable, that can cause a lower crosslinking density and lower the peroxide efficiency. But since the TMPTMA is immersible in rubber, the homo-polymerized oligomer can form a hard domain in rubber network. This hard domain can reinforce the rubber network and thus makes the rubber have both high tensile strength and high elongation. That’s can be identified via the Transmission electron microscopy (TEM), however, it will not include in this thesis since it still hard to stain the TMPTMA hard domain.

Table 3. 4 Summary of mechanical properties of compounds **1a**, **1b**, **2a-2i** and **3a**

Compound	**$\sigma_{100\%}$ (MPa)**	**$\sigma_{200\%}$ (MPa)**	**ε_b (%)**	**σ_b (MPa)**	**Toughness (10^6 J/m^3)**
1a	1.19±0.09	1.84±0.14	321±29	3.22±0.49	5.26±0.90
1b	0.98±0.16	1.10±0.22	780±20	1.96±0.35	12.16±0.10
2a	0.92±0.09	1.30±0.08	907±24	2.80±0.29	16.58±0.45
2b	0.83±0.04	1.12±0.07	1076±75	2.89±0.38	19.63±0.04
2c	1.14±0.15	1.60±0.21	740±82	4.25±0.91	17.59±0.63
2d	0.75±0.10	1.01±0.17	929±59	2.22±0.37	14.44±1.12
2e	1.08±0.16	1.59±0.20	751±60	5.47±0.09	19.49±0.06
2f	1.75±0.10	2.40±0.09	543±65	4.3±0.34	15.08±1.64
2g	0.94±0.04	1.16±0.04	1150±45	2.23±0.15	17.36±0.08

2h	0.89±0.12	1.28±0.08	841±103	3.13±0.29	16.34±0.31
2i	1.11±0.11	1.67±0.17	631±68	4.40±0.47	15.42±0.32
3a	1.41±0.14	2.08±0.18	459±41	4.33±0.55	11.78±0.02

($\sigma_{100\%}$, $\sigma_{300\%}$ is stress at 100%, 300% strain, respectively. ε_b is strain at break. σ_b is tensile strength of sample.)

3.5 Stress-relaxation test of sleeted compounds

When testing the tensile strength of 1a-1b, 2a-2i, and 3a, some of samples were flew during the strength time. That because the crosslink density is not sufficient enough to form a whole network, thus when applying force, some macromolecule chain was pulled out from the rubber network. After combing the result of tensile test and swelling test, compound 1a, 2c, 2e,2f,2i, and 3a were selected to test the stress-relaxation curves, which were shown in Figure 3.4.

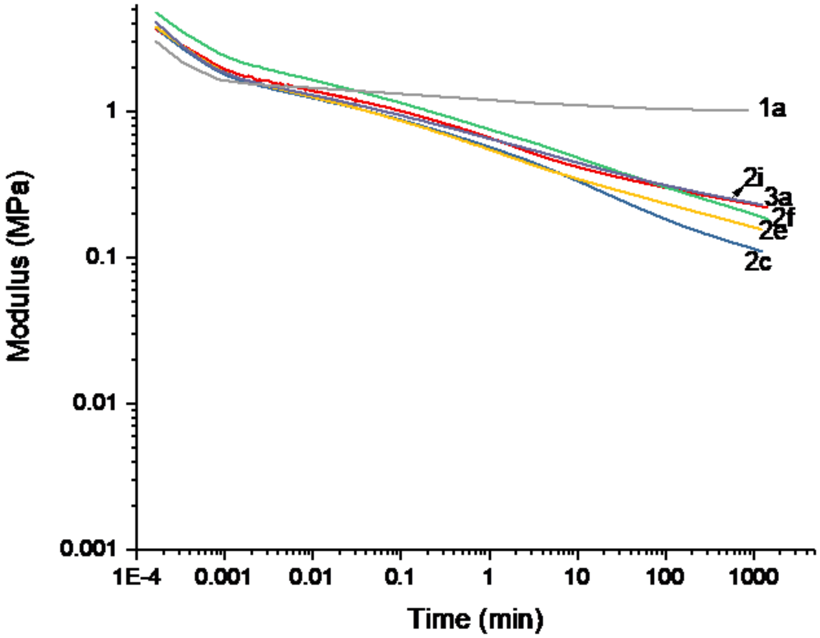


Figure 3. 4 Stress relaxation of compound 1a, 2c, 2e, 2f, 2i, and 3a

From Figure 3.4, after testing for 4 hours, almost all those compounds reach a near plateau relaxation modulus. The plateau modulus can represent the actually crosslink density of the crosslinked rubber. It is obvious that sulfur crosslinked butyl rubber (compound 1a) has the highest finite relaxation modulus, which is because lack of chain scission reaction. Peroxide cured bromo-butyl rubber (compound 3a) has the second highest finite modulus comparing with the rest of Et-g-IIR. The finite relaxation modulus of 2c, 2e, 2f, 2i is following the increasing loading of benzoyl peroxide and coagent TMPTMA.

The result of stress-relaxation is consisting with the explanation in tensile test part. All the three reactions (chain scission, crosslinking, coagent homo-polymerization), is uncontrollable during the crosslinking process. Combing the curing kinetic curves, the tensile results, swelling test and stress-relaxation test, it is obvious that increasing the load of peroxide, for example benzoyl peroxide (BPO), can increase the chance to generate crosslink. At the same time, after the peroxide decomposed and finishing H-abstraction or initiation, the rest of peroxide could increase the chance of chain scission. Meanwhile, since coagent TMPTMA has reactive acrylate group, it is unlikely to suppress the coagent homo-polymerization. But among all the result, compound 2e which loaded with 2 phr benzoyl peroxide and 10 phr TMPTMA has the best mechanical properties.

CHAPTER IV

CONCLUSION

The crosslinking behavior of ethyl propiolate grafted butyl rubber with different load of BPO and TMPTMA is investigated. The crosslink density and finite relaxation modulus are increased by increasing BPO and TMPTMA loading. However, since increasing benzoyl peroxide can increase chain scission reaction and coagent homo-polymerization. The mechanical properties especially tensile strength first increased with the increasing load of BPO (1-2 phr) then decrease with further increasing BPO (2-3 phr). After the cross-comparing of tensile strength, elongation, crosslink density and finite relaxation modulus, compound 2e which loaded with 2phr benzoyl peroxide and 10phr TMPTMA got the best result. Regardless the mechanism, with the help of coagent and proper chemical modification of butyl rubber, peroxide can be used to generate a crosslinked butyl rubber with high tensile strength and high elongation.

Further investigating of this study including the study of crosslinking mechanism and morphology study, including finding a proper way to detect the homo-polymerization of TMPTMA and finding a proper way to stain the TMPTMA oligomer. That will be finished in the following one or two months.

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