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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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DEGRADATION OF NATURAL RUBBER BY OXIDATION

Mr. Susawee Ondam

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ศึกษาการแตกตัวของยางธรรมชาติด้วยความร้อนและการออกซิเดชัน โดยการหาน้ำหนักโมเลกุลที่ลดลง ร้อยละของสารที่ระเหยได้ ร้อยละของสารที่สกัดได้ด้วยอะซิโตน ที่อุณหภูมิของการทำปฏิกิริยา 150–250 องศาเซลเซียสเป็นเวลา 2–8 ชั่วโมง และหาอัตราการแตกตัวเริ่มต้นของยางธรรมชาติที่ 2 ชั่วโมง พบว่าร้อยละของสารที่ระเหยได้และอัตราการแตกตัวเริ่มต้นเพิ่มขึ้นกับอุณหภูมิ เวลาที่ให้ความร้อน และความเข้มข้นของโซเดียมเพอร์บอเรต น้ำหนักโมเลกุลลดลง เมื่ออุณหภูมิสูงขึ้นและเวลาที่ให้ความร้อนนานขึ้น แต่ความเข้มข้นของโซเดียมเพอร์บอเรตไม่แสดงว่ามีผลอย่างชัดเจน ร้อยละของสารที่สกัดได้ด้วยอะซิโตนลดลงเมื่ออุณหภูมิและเวลาที่ให้ความร้อนเพิ่มขึ้น

ที่อุณหภูมิ 350 องศาเซลเซียส ยางธรรมชาติน้ำหนักโมเลกุลเฉลี่ยเริ่มต้นเท่ากับ 1,000,000 แตกตัวด้วยความร้อนร่วมกับโซเดียมเพอร์บอเรตที่มีความเข้มข้น 1.67 ส่วนในยางแห้ง 100 ส่วน เป็นเวลา 4 ชั่วโมง ภายใต้ความดันบรรยากาศได้สารประกอบอินทรีย์ที่มีน้ำหนักโมเลกุลต่ำ นำสารที่กลั่นได้ในช่วงอุณหภูมิ 120–270 องศาเซลเซียสมาวิเคราะห์ด้วยเครื่องแกสโครมาโตกราฟ–แมสสเปคโตรโฟโตมิเตอร์ พบว่าสารที่ได้มีน้ำหนักโมเลกุลเท่ากับ 136 ซึ่งเป็นสารในกลุ่มของลิโมนิน

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....
ปีการศึกษา 2543 ลายมือชื่ออาจารย์ที่ปรึกษา ....

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Thermal degradation and thermo-oxidative degradation of natural rubber were observed by heating at 150-250 $^{\circ}$C for 2-8 hours. After thermal treatments molecular weight reduction percentage volatile matters, percentage acetone extract, and initial rate of degradation at 2 hours were determined.

The results indicated an increase in percentage volatile matter and initial rate of degradation with temperature, heating time and concentration of sodium perborate. On a contrary, molecular weight distribution decreased with an increase in temperature and heating time. However, the data were inconclusive of how the concentration of sodium perborate effected the molecular weight distribution. The percentage acetone extract decreased when temperature and heating time increased.

When heating at 350 $^{\circ}$C, 1.67 phr sodium perborate for 4 hours under atmospheric pressure, natural rubber with original average molecular weight of 1,000,000 was thermally cracked into lower molecular weight organic fractions. The fractions were collected, distilled and the composition of light distillate (b.p.120–270 $^{\circ}$C) were identified by a GC–MS. The result showed a major component of molecular weight 136 which matched isomers of limonene.

Program Petrochemistry and polymer science Student's signature……………………………
Academic year 2000 Advisors signature…......................................

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CHAPTER 1

Introduction

1.1 General aspects

At present, Thailand is the largest natural rubber producer. The major rubber plantation areas are in the Southern and Eastern regions. Most of natural rubber producing countries produce natural rubber for export. In 1998, Thailand produced 2,075,950 tons of natural rubber, of which only 186,379 tons were used by the local rubber industry, the rest were exported. The major exported rubber products in 1998 are rubber tires (37 %) and rubber gloves (36 %), valued in excess of 25,000 million baht, or 75 % of total export. Since 1994, Thailand has been the largest producer of rubber in the world, followed by Indonesia and Malaysia. The world production of natural rubber is shown in Table 1.1

Table 1.1 World production of natural rubber (1994)

Country	Tons (x10^3)	% of world production
Thailand	1.50	27.62
Indonesia	1.35	24.86
Malaysia	1.07	19.71
India	0.425	7.83
China	0.325	5.99
Philippines	0.172	3.17
Sri Lanka	0.106	1.95
Others	0.482	8.87
Total	5.43	100.00

Total production of natural rubber in Thailand increased from 587,975 metric tons in 1983 to 1,530,941 metric tons in 1992. In the year 1992, domestic consumption of natural rubber in Thailand reached 118,372 metric tons, as shown in Table1.2 (Rubber Research Institute of Thailand, 1994). Commercial natural rubber can be classified into two major groups: solid natural rubber and latex concentrate. Thai producers produced 5 forms of dry rubbers listed in Table 1.2. Solid natural rubber can be produced from fresh field latex and skim latex. Solid natural rubber produced from skim latex can be divided into skim block and skim crepe. Solid natural rubber produced from fresh field latex can be divided into four groups: ribbed smoked sheet (RSS), air dried sheet (ADS), crepe rubber, and block rubber or Standard Thai rubber (STR), depending on its derived process (Figure 1.1). In each group of solid rubber, only small number indicates for less impurities or better grade; such as STR 5 is much than STR 20; and STR 5L (“L” means light color grade) usually requires bleaching.

Table 1.2: Different types of rubber in Thailand,1995.

Types of Rubber	% wt
Smoked sheet	66.00
Block rubber	18.30
Crepe rubber	0.73
Concentrated latex	9.48
Other rubber	5.46

Source : Southern Industrial Economics Center in Thailand

Table1.3 Thai Total natural rubber Production 1983-1992

	Exports	Domestic Consumption	Change in stock(+/-)	Imports	Production
1983	552,486	32,056	3,433	-	587,975
1984	595,585	31,653	1,951	-	629,189
1985	684,851	32,738	4,282	-	721,781
1986	755,157	39,550	-12,529	58	782,120
1987	873,212	47,081	1,373	108	921,558
1988	909,420	57,339	11,278	158	974,879
1989	1,100,580	77,601	265	58	1,178,388
1990	1,150,790	99,131	25,379	196	1,275,104
1991	1,231,945	103,107	5,632	88	1,340,596
1992	1,412,850	118,371	-268	12	1,530,941

Source : Thailand rubber statistic, 1994

Normally, natural rubber latex used in production is a result of concentration method and contains approximately 60% of dry rubber content (DRC). Natural rubber products (NRP) from latex have been used widely for over hundred years. This is attributed to the superior processing behavior and high physical strength of rubber. There are several products made from latex which can divided into two groups. The first is NRP made from concentrated latex such as gloves, condom, tip catheters, endotracheal tubing latex balloon, baby bottle nipples, and dental cofferdams. The second is NRP made from solid rubber such as tire, shoes, adhesives, elastic rubber, and medical products.(Figure 1.2)

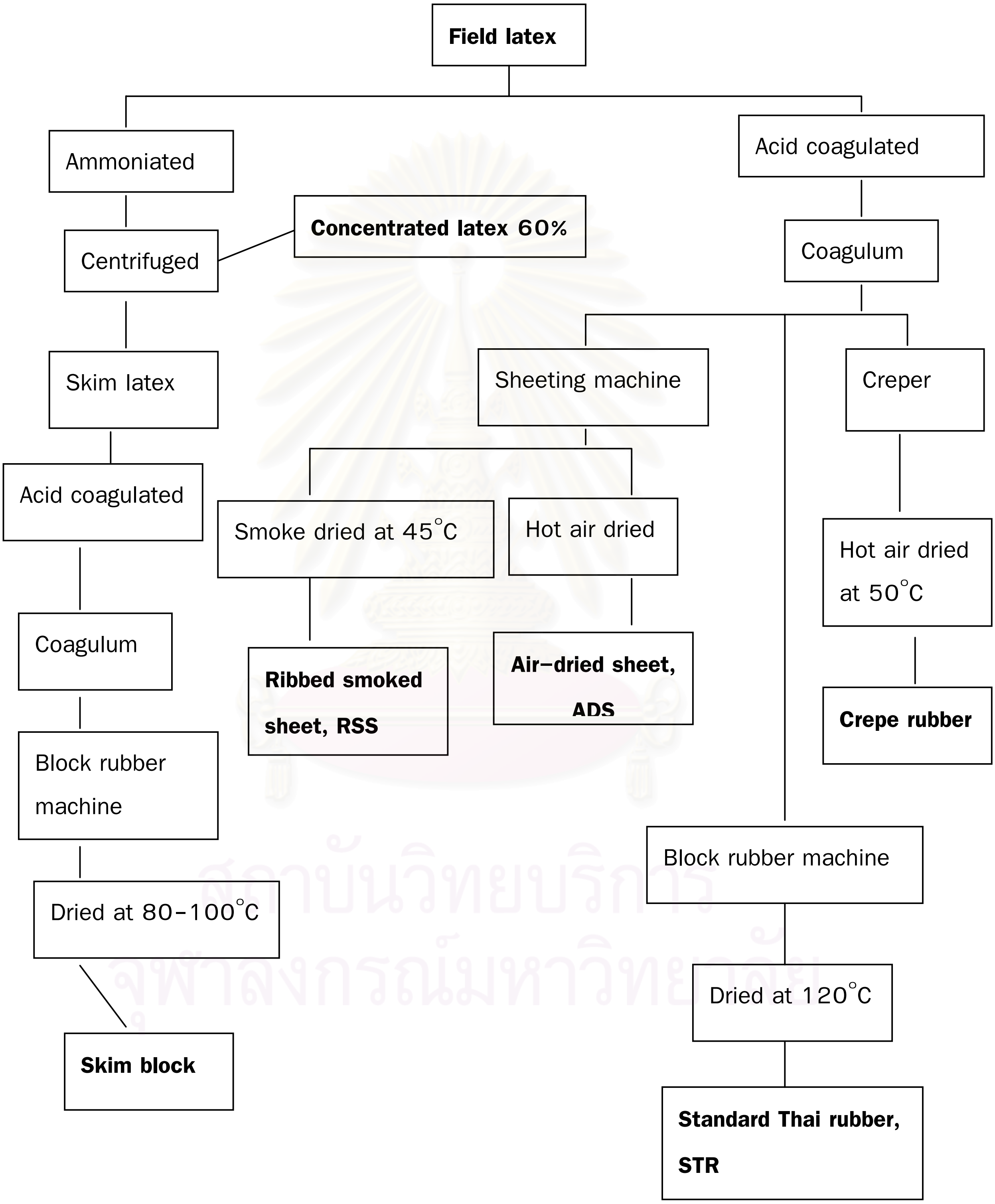


Figure 1.1: Natural rubber production process in Thailand (From ParaRubber Bulletin, Thailand 7, 1986)

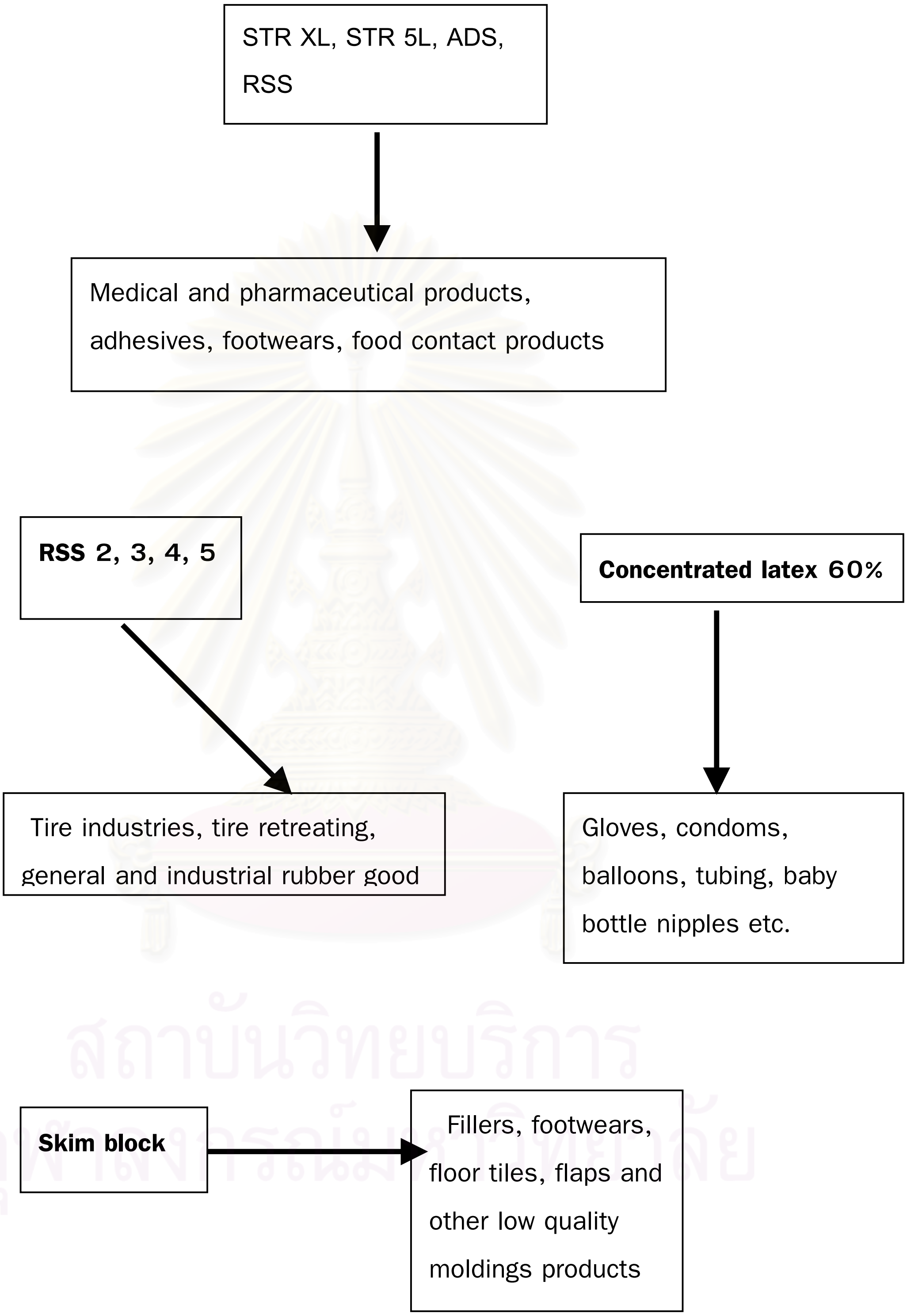


Figure 1.2: Natural rubber products in Thailand (From Para Rubber Bulletin, Thailand 7, 1986)

Table 1.4 Domestic consumption of natural rubber in Thailand,1988-1992.

Unit : metric tons

Type of product	1988	1989	1990	1991	1992
Tyre and tube for motorcars and airplanes	20,559	32,348	38,411	42,069	50,597
Tyre and tube for motorcycles and bicycles	3,673	4,737	6,567	6,437	6,342
Re-treading	1,624	1,213	1,078	1,815	2,029
Belt	287	498	502	463	613
Shoe layer	1,612	821	1,955	2,127	2,768
Hose	572	624	5,215	787	1,397
Accessory parts for motor Vehicle	2,283	2,318	3,315	3,436	3,795
Husk cracker for rice mill	123	149	254	196	235
Battery body	484	589	519	529	570
Canvas shoes and foam sandal	5,693	6,147	7,504	7,620	8,678
Rubber band	4,612	10,063	11,378	11,544	11,902
Elastic	1,256	4,028	4,756	5,469	6,824
Balloon	75	132	101	118	146
Foam products	185	285	331	749	579
Scientific instruments	30	30	-	-	-
Carpet backing	124	354	395	440	498
Doll and condom	153	239	33	448	726

Table 1.4: Domestic consumption of NR in Thailand, 1988-1992 (continued)
Unit : metric tons

Type of product	1988	1989	1990	1991	1992
Wind screen fixing rubber	84	86	108	-	-
Cushion foam	171	159	578	-	-
Fishery float	16	9	91	-	-
Glue tape for electric wire	165	245	263	433	740
Cover					
Glove	11,813	11,825	14,008	15,342	16,882
Football	-	-	601	926	1,304
Teat	-	-	-	1,594	753
Rubber	-	-	-	5	1
Compound rubber	-	-	-	227	327
Others	495	344	1,138	266	653
Total	57,339	77,601	99,131	103,108	118,372

Source : Thailand rubber statistic,1994

In 1994, Thailand exported 131,888 tons and the remaining 32,736 tons was used locally. The majority was exported to the USA, Taiwan, Germany and Singapore. The majority of Thai export rubber products are ribbed smoked sheets of comparatively low price and quality. It is therefore necessary for Thailand to develop new products from natural rubber. Special rubbers are produced to meet consumers' demands requiring suitable properties for some special applications. New products can be developed from natural rubber, i.e. adhesive, fuel oil, surfactant etc. However, knowledge of chemical reactions on reforming natural rubber is required. Development of new products from natural rubber will lead to added value for natural rubber.

1.2 Objectives of this study

1) To investigate changes in molecular weight of natural rubber due to thermal degradation catalyzed by peroxide.
2) To investigate the effect of peroxide quantity on degradation rate.
3) To partially identify the light fraction of reaction product.

1.3 Scope of the research project

1) Field latex will be heated and dried followed by thermal degradation at 150, 200 and 250 °C. The effect of temperature on average molecular weight and molecular weight distribution was observed by gel permeation chromatography.
2) The facilitation of sodium perborate (0,1.67, 3.3 and 3,5 phr) on degradation was studied.
3) Effect of heating medium by adding paraffin oil (25 g and 10 g per 25 g concentrated latex) was studied.
4) Two types of peroxide, one soluble in oil (benzoyl peroxide) and another soluble in water (sodium perborate), on degradation rate were determined.
5) Light fractions of degraded product at high temperature were partially identified by determination of functional groups using FT-IR, FT-NMR and GC-MS.

CHAPTER 2

LITERATURE REVIEWS

2.1 Characteristics of natural rubber latex

Natural rubber can be isolated from more than a thousand different species of plants. The fresh latex used commercially is tapped from the para rubber tree which is known by scientific name as Hevea brasiliensis. It is milky white or slightly yellowish opaque liquid and contains 25 to 50 % dry rubber content (DRC). The chemical and physical characteristics depend on clones of rubber, age of plant, tapping intensity, soil characteristics and season of tapping. The composition of fresh latex is shown in Table 2.1

Table 2.1: The composition of fresh latex [1]

Composition	Percent
Rubber Hydrocarbon	30.0 – 45.0
Proteinous substance	2.0 - 2.5
Water	58.5
Neutral lipids	1.4
Phospholipids	0.6
Ash	0.5
Inositols and carbohydrates	1.6
Other nitrogenous Compounds	0.3

The latex contains rubber particles of different diameters from 0.02 μm to 3 μm. The rubber particles are in an ambient serum (C – serum) with pH 6.9 .

The rubber particles are mostly spherical with small amounts of pear-shaped particles. The rubber particles in fresh latex are protected by a complex film containing proteins and lipids. Each particle soluble in water and stable with a negatively charged surface.

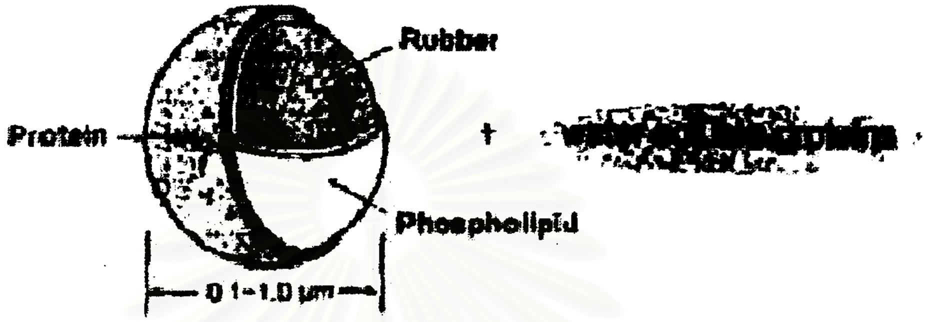


Figure 2.1: Presumed structure of solid rubber particle [1]

Fresh latex can be separated into three fractions by ultracentrifugation:

1) The top layer is rubber particles phase with a small layer of the Free–Wyssling complexes below it.
2) The middle layer is the C–serum phase which contains mostly water. The serum phase contains small amounts of soluble compounds including inositols, carbohydrate, amino acids, proteins, inorganic anions and metal ions.
3) The bottom fraction contains mostly lutoids comprises 10-20 % volume of the latex and small amounts of other non–rubber particles. Lutoids are spherical membrane–bounded bodies typically 2–5 µm in diameter. These lutoids are heavier than rubber particles and form bulk at the bottom fraction.

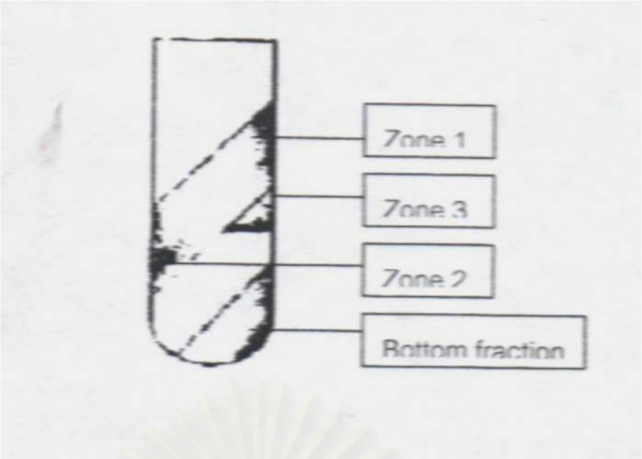


Figure 2.2: High – speed centrifugation of natural rubber latex, Moir, 1959

2.2 Biosynthesis mechanism of natural rubber [2]

In 1960's the biochemical studies about the chain extension step of rubber formation proceeds by successive addition of isopentenyl diphosphate (IDP) to pre-existing rubber particles. It was proposed that rubber formations initiate from dimethylallyl diphosphate (DMADP) which is formed by isomerization of IDP. The biosynthesis mechanism of natural rubber presents in Figure 2.3

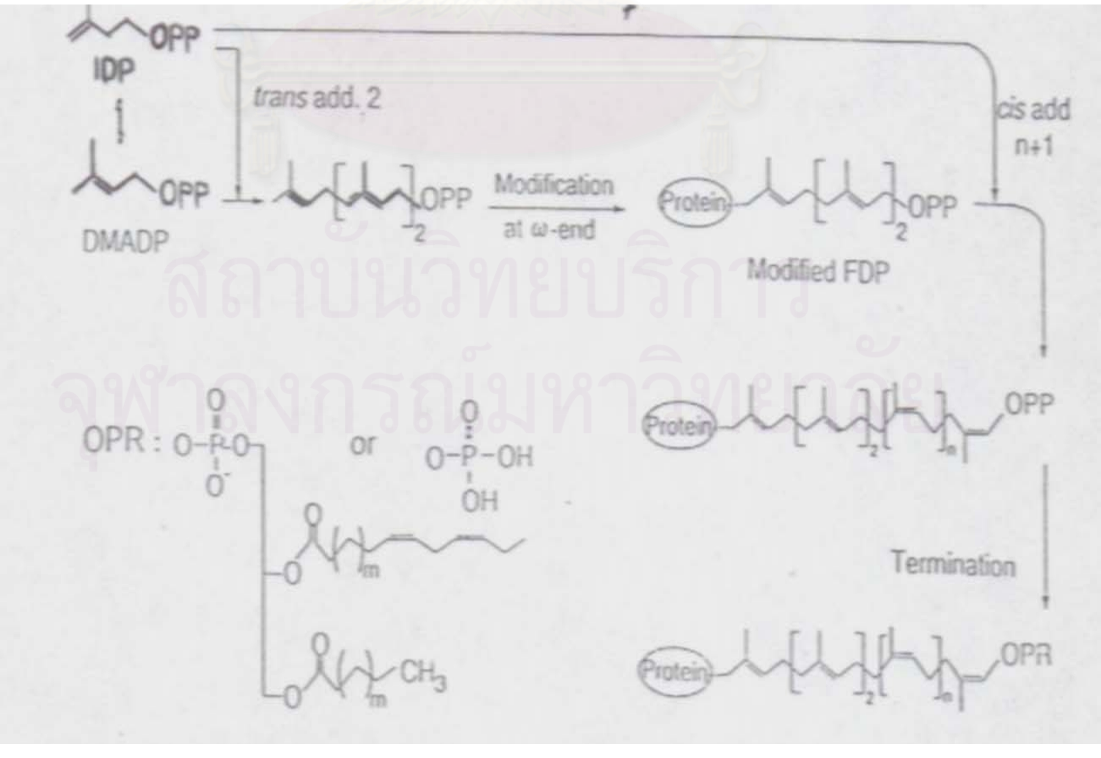


Figure 2.3: Presumed steps of rubber formation in H. brasiliensis. [2]

Condensation reactions: A clue for polymerization [2]

It is certain to regard rubber biosynthesis is a condensation reaction. Again, as with acetyl–CoA, the bifunctional nature of the active isoprene building block is a key to the polymerization reaction. For IDP, this bifunctionality resides in the nucleophilic reactivity of the 4–double bonds and the potent electrophilic character of the diphosphate ester.

In rubber biosynthesis, the first step has been postulated to be the isomerization of IDP to DMADP via the enzyme isopentenyl diphosphate 4–isomerase. With the formation of DMADP, the electrophilic reactivity of the precursor IDP is realized. The elimation of a proton leads to the first condensation product, an allyllic diphosphate containing ten carbon atoms. This homologous allyllic diphosphate by acquisition of another IDP is converted into a C_{15}–compound. The repetition of this process eventually leads to high molecular–weight rubber.

The stereochemical work done by Popjak and Comforth, gave the conclusion that no free carbonium ions are generated from the allylic diphosphate and that condensation is accompanied by the concerted removal of a proton. It was found that an inversion of configuration at C–1 of the allylic diphosphate occurs during chain growth. Cornforth and Popjak suggested this observation was an S_N2 – mechanism for the condensation in which the diphosphate ion is displaced in synchronization with attachment of a new isopentenyl unit. Without neighboring group effects, such reactions occur with inversion of configuration. The detailed chemical mechanism of rubber synthesis, as depicted in figure 2.3, forces one to postulate an electron–donating group X, that is temporarity attracted at C–3 (=CH-). The chemical nature of X cannot be specific. It may be a group on the enzyme, or possibly the diphosphate anion of IDP itself, as suggested by Johnson and Bill. The polymerization of natural rubber from low molecular weight to high molecular weight was reacted on rubber particle surface only. The site, where polyprenyl transferase (PT) or rubber transferase (RuT) shows activity, is the interphase between serum. Rubber particles appear to facilitate the production of rubber by a system, in which the hydrophilic substrates DMADP and IDP are converted into a lipophilic end–product. Lynen has illustrates a hypothetical scheme outlining the events at the interphase, which is given in Figure 2.4. It was assumed that the growing hydrocarbon chain of rubber diffuses into the interior of the rubber droplet, while the hydrophilic diphosphate end–group remains in the serum phase where it can react with IDP by bound to the active site of the RuT. In this way, deposition of the enzyme surface and its subsequent inhibition is avoided. The association between rubber transferase and rubber particles may be rather stable.

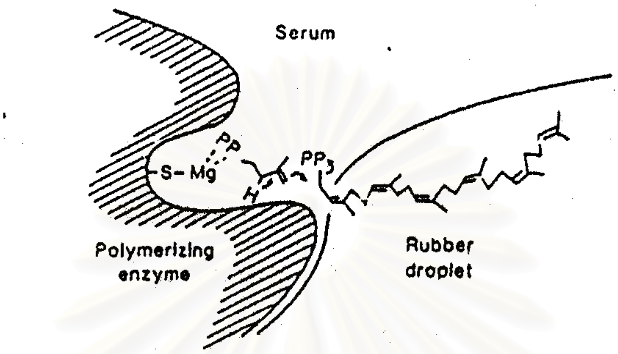
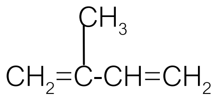


Figure 2.4: Hypothetical scheme of the chain extension mechanism on the surface of a rubber particle [2]

2.3 Structure and molecular weight of natural rubber

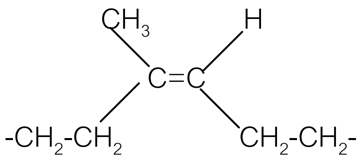
The structural formula of natural rubber molecules are $(C_5H_8)_n$, where the isoprene monomer is represented by formula, C_5H_8 where n is about 20,000. The empirical formula for the natural rubber molecule appears to have been first determined by Faraday who reported his finding in 1826. He concluded that carbon and hydrogen were the only elements present and his results corresponded to the formula C_5H_8. While this result was obtained, using a product which contained associated non–rubbery materials, subsequent studies with highly purified materials have confirmed Faraday's conclusion.

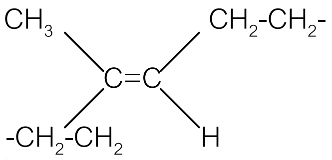
The isoprene was found to have the formula C_5H_8, for which Tilden proposed the structure [1].



$$CH_2{=}\overset{\overset{\large CH_3}{|}}{C}\text{-}CH{=}CH_2$$

The linear structure proposed by Pickles provided for the possibility of structure isomerism with both cis– and trans– repeating units.





It was known that this is the major hydrocarbon component of both gutta percha and balata (at the time important in belting, submarine cable, golf ball and container applications) was a polyisoprene which when reacted with bromine and ozone gave similar results to those obtained with natural rubber. It was tempting to suggest that one isomer was that of gutta percha and balata and the other that of natural rubber. The earlier work of Staudinger suggested that the trans–isomer was natural rubber and gutta percha, *the cis*-. However later studies of X–ray fiber diagrams of stretched rubber led Meyer and Mark to the view that natural rubber was the cis–polymer, a view reinforced by Bunn (1942) which elucidated the structure and unit cell of the crystalline stretched rubber molecules.

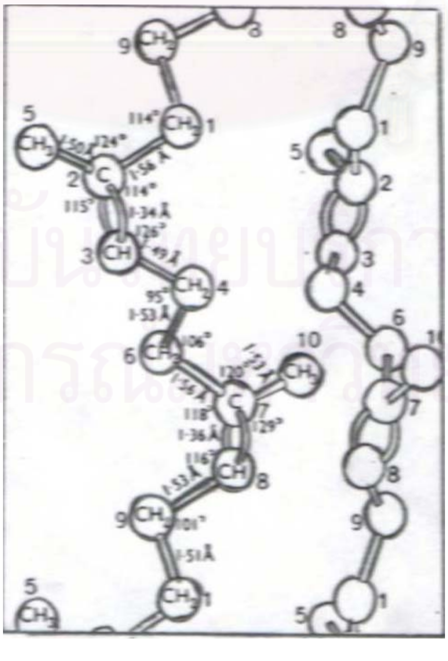
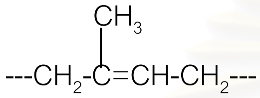


Figure 2.5: Unit cell structure, of the natural rubber molecule. (From Bunn, 1942)

The possibility that the natural rubber molecule might contain a mixture of cis– and trans- groups was considered to be unlikely because such a mixed polymer would have an irregular structure and be unable to crystallize in the manner of natural rubber. Infrared studies have subsequently confirmed that natural rubber was the cis– polymer.

The natural rubber was at least 97% cis–1,4–polyisoprene. The absence of measurable amounts of 1,2–structure and an infrared band at 890 cm^{-1} was at one time thought to be due possible to the products of a 3,4–structure.



$$\text{---}CH_2\text{-}\overset{CH_3}{\overset{|}{C}}{=}CH\text{-}CH_2\text{---}$$

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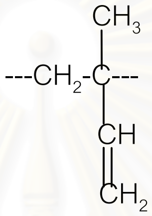

$$\text{---}CH_2\text{-}\overset{CH_3}{\overset{|}{\underset{\underset{\underset{CH_2}{\|}}{CH}}{\underset{|}{C}}}}\text{---}$$

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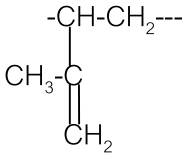


3, 4-

Time–averaging techniques using high resolution NMR which are capable of detecting 3,4–groups at concentrations of less than 0.3 % have however failed to establish the existence of any such moiety and have also failed to show up any trace of trans–materials. The conclusion must therefore be that the molecule is more than 99% cis–1,4–polyisoprene. Since all the evidence points to the conclusion that the natural rubber molecule is not obtained in nature by the polymerization of isoprene the absence of detectable pendant groups as would be produced by 1,2– and 3,4– addition is hardly surprising.

Gel phase

NR consists of 5–50 % gel phase which can be classified into two types macrogel and microgel. Macrogel is insoluble in solvents but microgel can be soluble in solvents; depending on clone of rubber. These gels cause an increasing in the bulk viscosity of rubber. Microgel (about 1–47%) causes crosslinking between rubber molecules within the rubber particle (Freeman, 1954), while the macrogel (about 2–17.5%) is associated with storage hardening of dry rubber (Wood, 1952). Freeman has shown that rubbers with high microgel content and macrogel content have higher bulk viscosity, but bulk viscosity is independent on macrogel content at level lower than 5 %.

The hardening reactions occur from crosslinkings between rubber molecules in the main rubber chains (as indicated by the increase in mooney viscosity). These crosslinking involve aldehyde or carbonyl groups in the rubber molecules (Bloomfield, 1951; Sekhal, 1961 and 1962) and aldehyde groups in the non–rubber phase, including some amino acid (Subramaniam, 1975; Sekhar, 1962; Gregory and Tan, 1976). The variation of viscosity is due to many factors, clonal rubber, average molecular weight, microgel and gel content and non–rubber constituents.

Protein and its effect [2]

The total protein content of fresh latex is about 1.0-1.5%. About 20% of total protein is adsorbed on the rubber particles, the other 20% is associated with the bottom fraction. The rest are soluble protein in aqueous serum phase. The proteins adsorbed on the rubber particles have not been studied in much details due to the difficulties in removing them from the rubber particles. Proteins do not confer any significant advantages. The presence of proteins in the natural rubber has been reported to have resulted in some undesirable properties such as poor creep and stress–relaxation reduced modulus and increasing sensitivity to water and moisture.

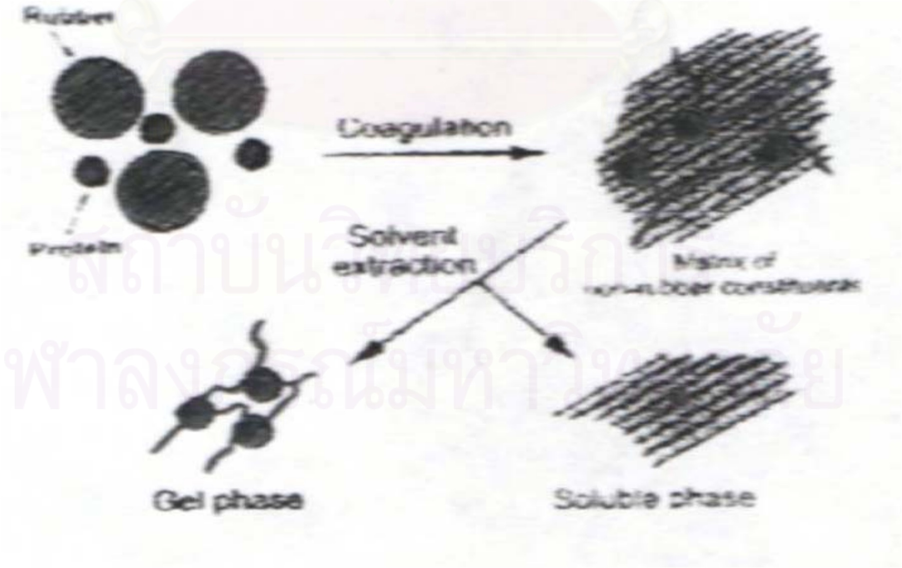


Figure 2.6: Schematic representation of gel phase in latex and in rubber (Allen et al., 1963)

2.4 Molecular weight and molecular weight distribution [1]

In 1971 gel permeation chromatrography (GPC) was used to determine the molecular weight and molecular weight distribution (MWD) of rubbers.

Rubber from Hevea brasiliensis is a high molecular weight polymer with broad molecular weight distribution. Hevea rubber in freshly tapped latex has been confirmed to have a bimodal distribution by GPC analysis. The distributions of various clonal Hevea rubbers are classified into three types: one where the distinctly bimodal distribution with nearly equal peak height, and two where the bimodal distribution with small low molecular weight peak, and the other where skewed unimodal distribution with shoulders. Differences in molecular weight distribution can be observed in commercial Hevea rubbers as shown in Figure 2.7 (A). The average molecular weight is M_w = 1.6–2.3x10^6 and M_n = 2.0–5.2x10^5; the molecular weight of polydispersity cab be expressed by M_w/M_n is extremely wide ranging from 2.8 to 10.0. On the other hand, rubber from guayule and synthetic cis–polyisoprenes made with a Ziegler initiator system show a unimodal distribution; typical GPC curves are shown in Figure 2.7 (B)

The broad molecular weight distribution of Hevea rubber is estimated to be associated with branching and crosslinking reactions through some special functional groups.

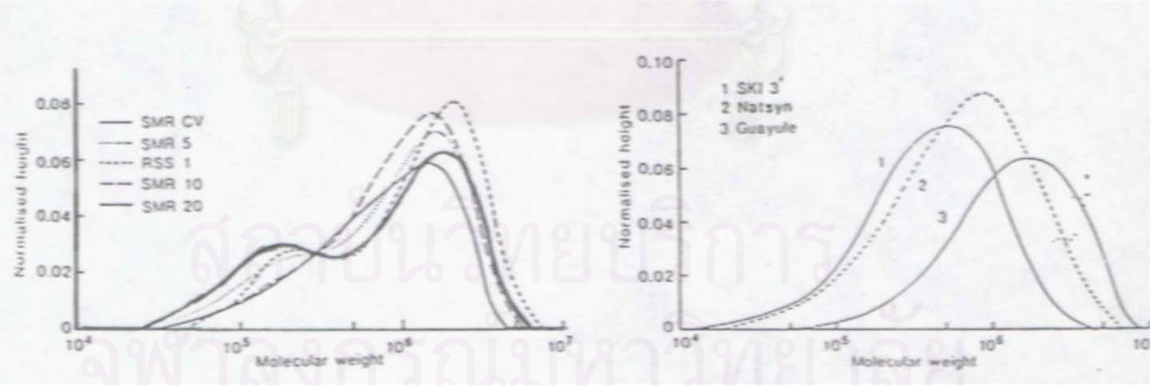


Figure 2.7: Typical molecular weight distribution of (A) commercial Hevea rubbers and (B) guayule rubber and synthetic cis-polyisoprenes.[1]

2.5 Usefulness of natural rubber [3,4]

Natural rubber is a viscoelastic material. It has viscosity similar to that of liquid and it has elasticity similar to that of solid. Apart from these properties, natural rubber has many properties of interest. Which:

1) Natural rubber has its properties improved by adding filler such as sulfur, accelerator or reinforcement.
2) Natural rubber has high elasticity and high impact and abrasion resistance and good tear resistance.
3) Natural rubber can prevent the permeation of gas.
4) Natural rubber is a good insulator.
5) Natural rubber can undergo many reactions, such as chlorination or cyclization or epoxidation or degradation.

The reactions of natural rubber are represent in the block diagrams below:

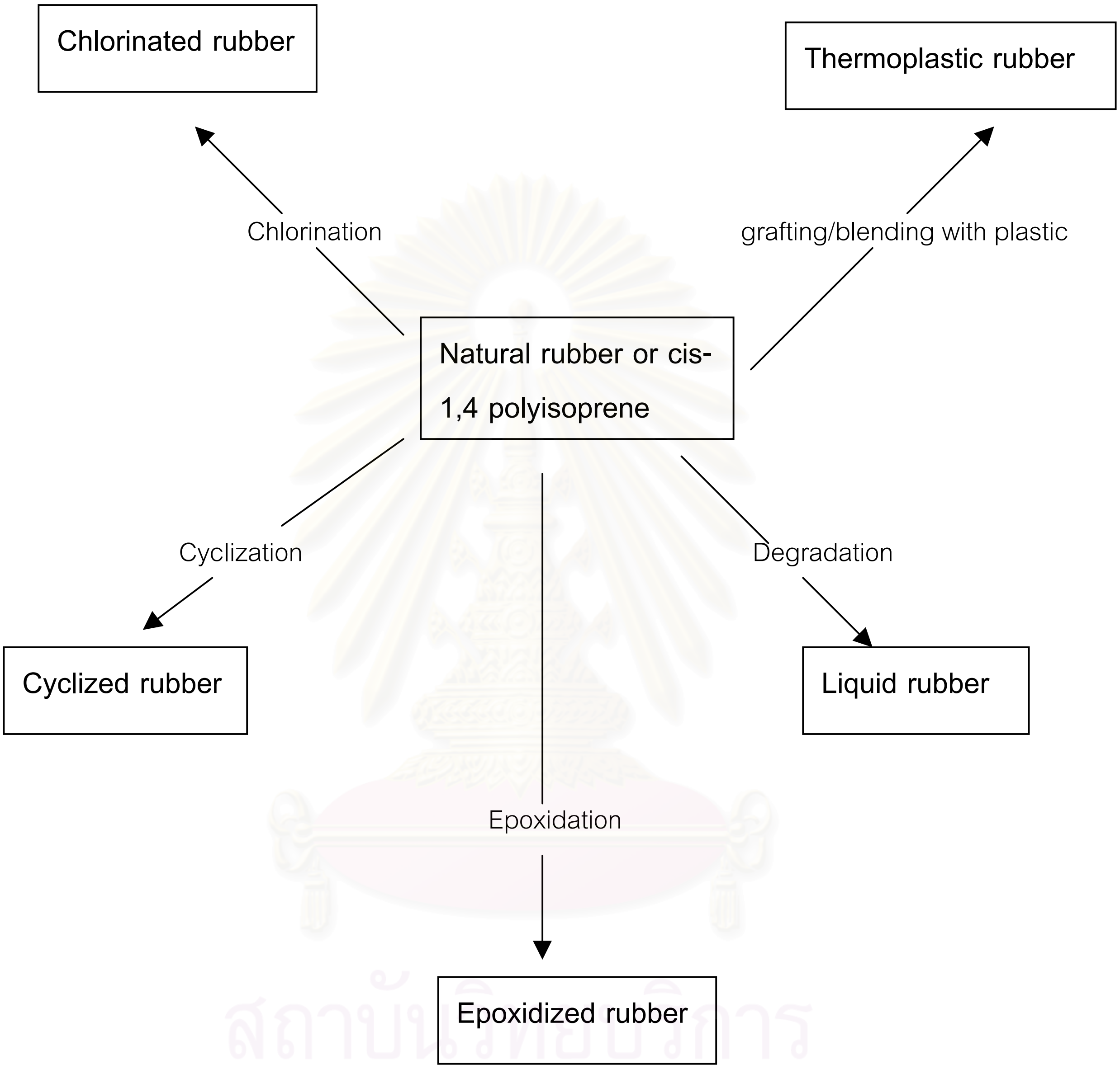


Figure 2.8: Block diagram represents exchanged structure of natural rubber by chemical reactions

2.6 Degradation of natural rubber

Polymer degradation is the collective name given to various processes which degrade polymer. Degradation is a reversal of polymerization process. For most chain polymerizations there is some temperature at which the reaction becomes a reversible one, that is the propagation step should be written as an equilibrium reaction

$$M_n^{\cdot} + M \underset{k_{dp}}{\overset{k_p}{\rightleftarrows}} M_{n+1} \qquad 2.1$$

Where k_{dp} is the rate constant of the reverse reaction-termed depolymerization or depropagation. The overall effect of temperature on polymerization is complex due to the presence of this propagation-depropagation equilibrium. When the temperature is initially increased for the polymerization of a monomer, the polymerization rate increases as k_p increases. However, at higher temperatures the depropagation rate constant k_{dp}, which was initially zero, increases and becomes significant with increasing temperature. Finally, a ceiling temperature [5] T_c is reached at which the propagation and depropagation rates are equal. At T_c, the net rate of polymer production is zero. For many of the alkene monomers, the equilibrium position for the propagation-depropagation equilibrium is far to the right under the usual reaction temperatures employed, that is, there is essentially complete conversion of monomer to polymer for all practical purposes. The successful polymerization of a previously unpolymerizable monomer is often simply a matter of carrying out the reaction at a temperature below its T_c. Interestingly, it should not be assumed that a polymer will be useless above its ceiling temperature. A dead polymer that has been removed from the reaction media will be stable and will not depolymerize unless an active end is produced by bond cleavage of an end group or at some point along the polymer chain. When such an active site is produced by thermal, chemical, photolytic, or other means, depolymerization will follow until the monomer concentration becomes equal to $[M]_c$ of the particular temperature. The thermal behavior of many polymers, however, is much more complex. Degradative reactions other than depolymerization will often occur at temperatures below T_c. In the simplest case, depolymerization consists of initiation at chain ends, depropagation, and termination. In the depropagation step, monomer is unzipped rapidly from the activated chain ends. The main characteristic of degradation processes with dominating depolymerization character is high monomer yield. Depolymerization leading to high purity monomers may be exploited for practical production of such materials. Degradation may be happen during every phase of a polymer's life, i.e.,during its synthesis, processing, and use. In degradation of polymers are composed of monomeric units which are joined by chemical bonds which either are in the main chain of the macromolecule or connect various atoms or side groups to it. Side groups, if they are present, contain additional chemical bonds. All of these bonds may be reaction sites in polymer degradation, and various energy sources may be effective in supplying the energy necessary to break the bonds. The bond energies are manifold and depending not only on the kind of atoms connected by the bond but also on the chemical and physical characteristics surrounding the bond. The most important types of energy that cause polymer degradation are heat, mechanical energy, and radiation. As a result of degradation processes, initiated and completed by the above factors or their combination [6], the internal properties as well as the external appearance of the polymers may change. Chain scission and cross–linking lead to a change of molecular weight distribution; oxidation and other chemical reactions, in the side chains too, cause changes in chemical composition. The dissociation energies of the various bonds in the polymer may determine the course of the degradation: the process always begins with the scission of the weakest available bond or with an attack at this site, and the first step usually determines further direction of the process. Other components of the chemical structure, such as steric factors, stability of the intermediates, or the possibility of their resonance stabilization, may also have great influence on degradation. Such factors may even change the value of the bond dissociation energy [7].

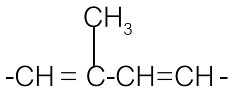
Table 2.2: Bond Dissociation Energies of Various Single Bonds [5].

BOND BROKEN A-B	BOND DISSOCIATION ENERGIES (kcal/mol)
C_2H_5-H	99
n-C_3H_7-H	98
t-C_4H_9-H	91
CH_2=$CHCH_2$-H	82
C_6H_5-H	103
$C_6H_5CH_2$-H	83
C_2H_5-CH_3	83
n-C_3H_7-CH_3	83
t-C_4H_9-CH_3	81
C_6H_5-CH_3	94
$C_6H_5CH_2$-CH_3	72
CH_3-Cl	84
C_2H_5-Cl	81
CH_2=$CHCH_2$-Cl	65
CH_3-F	108
C_2H_5-F	106
HO-OH	51
t-C_4H_9O-OH	36

Table 2.3 Bond Dissociation Energies of Some CH_3-R Bonds [5].

-R	Bond Dissociation energies (kcal/mol)
$-CH_3$	88.4
$-C_2H_5$	84.5
$-n-C_3H_7$	84.9
$-n-C_4H_9$	84.7
$-I-C_3H_7$	83.8
$-t-C_4H_9$	80.5
$-CH_2-CH=CH_2$	73.6
$-CH(CH_3)-CH=CH_2$	72.3
$-CH_2-C_6H_5$	71.9
$-CH(CH_3)-C_6H_7$	68.7
$-C(CH_3)_2-C_6H_5$	65.7
$-CH=CH_2$	93.7
$-C_6H_5$	94
$-CH_2-OH$	82.1
$-CH_2-(CO)-CH_3$	79
$-CH_2-CN$	77.1

Natural rubber is a high molecular weight hydrocarbon polymer consisting mainly of the isoprene unit (C_5H_8). It has two double bonds. The structure of polyisoprene is show below:



$$-CH=\overset{\overset{\large CH_3}{|}}{C}-CH=CH-$$

From the structure of polyisoprene, we know that the structure of natural rubber is polyene. Natural rubber can depolymerize in the same general way as polyene. Alkene was reacted at double bond, where reactivity is high. The reactivity of alkenes presents dealing with double bond reactivity in the particular environment of a long chain molecule. The main points to be borne in mind are itemized below [8].

1) The peculiar reactions of alkenes stem entirely from the presence of the double bond although at points away from the double bond the alkene can also behave as an alkane.
2) The double bond consists of a strong bond and a weak bond.
3) The bond's electrons, which lie in electron clouds above and below the plane of the atoms are less tightly held than the bond electrons and may be considered as a source of electrons. In effect the double bond acts like a base.
4) These bond electrons will tend to react with substances deficient in electrons, i.e. agents attracted to electrons (electrophilic agents, acids), by the process of electrophilic addition.
5) Free radicals are also attracted to electrons so that alkenes may also react with free radicals. Reactions affected by the presence of oxygen, peroxides, ultra-violet light.

2.7 Chemical and thermodynamic aspects of depolymerization [5]

Depolymerization can be the dominating degradation process of a polymer if

A) Initiation by main chain scission is a necessary condition of depolymerization because this process produces the terminal active site capable of depropagation.

B) The terminal radicals formed in the initiation step or in the depropagation steps must be stable enough to not participate in various side reactions such as chain transfer.

C) The activation energy of depropagation is the sum of the activation energy of polymerization propagation and the heat of polymerization. The lower the polymerization heat, the lower is the activation energy of depropagation, thus the higher is the probability of depolymerization.

For all of these materials it is possible to postulate a chain reaction of the following type, where RH represents a hydrocarbon molecule.

Initiation:

$$RH \longrightarrow R^{\cdot} \tag{2.2}$$

Propagation:

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot} \tag{2.3}$$

$$RO_2^{\cdot} + RH \longrightarrow ROOH + R^{\cdot} \tag{2.4}$$

$$ROOH \longrightarrow RO^{\cdot}, RO_2^{\cdot} \tag{2.5}$$

Termination:

$$2R^{\cdot} \longrightarrow R-R \tag{2.6}$$

$$R^{\cdot} + RO_2^{\cdot} \longrightarrow ROOR \tag{2.7}$$

$$2RO_2^{\cdot} \longrightarrow \text{Non - radical products} \tag{2.8}$$

Figure 2.9 Simpliified general scheme of alkene oxidation [8]

The oxidative degradation of polymers is a free radical chain reaction. An important difference from some other chain reaction is that besides the usual three steps, i.e., initiation, propagation, and termination. Two additional important steps must be considered: conversion of the formed hydrocarbon radicals to peroxy radicals (this is the main oxygen consuming reaction) and degenerate chain branching (this is the reaction responsible for the autoacceleration character of the process). A scheme including the most important steps in polymer oxidation is shown in Figure 2.10. It is to be noted that this is not a complete oxidation scheme; there are several other reactions which may take place during the oxidation of a polymer, depending on the chemical structure of the investigated polymer, the type and amount of contaminants and additives present in the system.

Initiation :

$$RH + O_2 \longrightarrow R^{\cdot} + HO_2^{\cdot} \qquad 2.9$$

$$\text{Initiator} \longrightarrow 2R^{\cdot\cdot} \qquad 2.10$$

$$R^{\cdot\cdot} + RH \longrightarrow R^{\cdot} + R^{\cdot}H \qquad 2.11$$

$$HO_2^{\cdot} + RH \longrightarrow R^{\cdot} + H_2O_2 \qquad 2.12$$

Radical conversion (stabilization) :

$$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot} \qquad 2.13$$

Chain propagation:

$$RO_2^{\cdot} + RH \longrightarrow R^{\cdot} + RO_2H \qquad 2.14$$

$$RO_2^{\cdot} + RH \longrightarrow R^{\cdot} + \text{products} \qquad 2.15$$

Degenerate chain branching:

$$ROOH \longrightarrow (RO^{\cdot} + HO^{\cdot}) + (RO + H_2O) \qquad 2.16$$

$$RO^{\cdot} + RH \longrightarrow R^{\cdot} + ROH \qquad 2.17$$

$$HO^{\cdot} + RH \longrightarrow R^{\cdot} + H_2O \qquad 2.18$$

Termination:

$$R^{\cdot}, RO_2^{\cdot}, \text{etc.} \longrightarrow \text{products} \qquad 2.19$$

Figure 2.10: Simplified general scheme of polymer oxidation [9]

The general scheme of polymer oxidation (Figure 2.10) can be further simplified when our intention is merely the kinetic description of the main characteristics of the process. Such characteristics are the time dependence of oxygen absorption, and the temperature, pressure, and concentration dependence of the degradation rate. Of course, there are many other important features of polymer degradation such as the change of MWD, the formation of volatile products, and the change of polymer composition due to the built-in oxygen containing steps. At high oxygen pressures present with the scheme shown in Figure 2.11 and at low and medium oxygen partial pressures presence with the scheme in Figure 2.12.

Initiation:

$RH + O_2 (+RH + 2O_2) \longrightarrow 2RO_2^{\cdot} + H_2O_2$ 2.20

$Initiator (+2RH + 2O_2) \longrightarrow 2RO_2^{\cdot} + 2R'H$ 2.21

Radical conversion:

$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}$ 2.22

Chain propagation:

$RO_2^{\cdot} + RH (+ O_2) \longrightarrow RO_2^{\cdot} + RO_2H$ 2.23

$RO_2^{\cdot} + RH (+ O_2) \longrightarrow RO_2^{\cdot}$ + products 2.24

Degenerate chain branching:

$ROOH(+ 2RH + 2O_2) \longrightarrow 2 RO_2^{\cdot} + ROH + (RO + H_2O)$Termination : 2.25

$RO_2^{\cdot} \longrightarrow$ Products 2.26

$RO_2^{\cdot} + RO_2^{\cdot} \longrightarrow$ Products 2.27

Figure 2.11 Simplified general scheme of polymer oxidation at high oxygen pressures [9]

At low and medium oxygen partial pressures presence with the scheme in figure 2.12

Initiation:

$RH + O_2 (+RH) \longrightarrow 2R^{\cdot} + H_2O_2$ 2.28

$Initiator (+2f'RH) \longrightarrow 2R^{\cdot} + 2R'H$ 2.29

Radical conversion :

$R^{\cdot} + O_2 \longrightarrow RO_2^{\cdot}$ 2.30

Chain propagation:

$$RO_2^{\cdot} + RH \longrightarrow R^{\cdot} + RO_2H \qquad 2.31$$

$$RO_2^{\cdot} + RH \longrightarrow R^{\cdot} + \text{products} \qquad 2.32$$

Degenerate chain branching:

$$ROOH\ (+\ 2RH) \longrightarrow 2R^{\cdot} + ROH + (RO + H_2O) \qquad 2.33$$

Termination:

$$R^{\cdot} \longrightarrow \text{Products} \qquad 2.34$$

$$RO_2^{\cdot} \longrightarrow \text{Products} \qquad 2.35$$

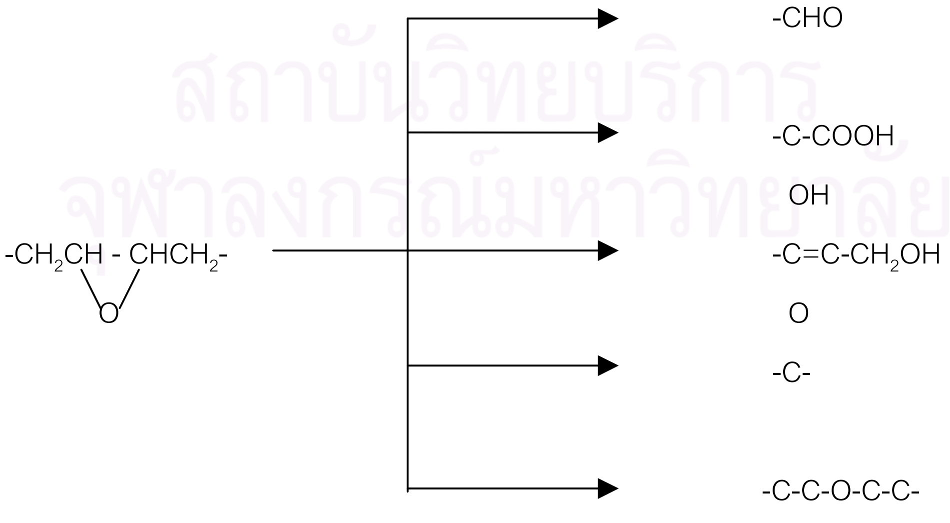
$$R^{\cdot} + R^{\cdot} \longrightarrow \text{Products} \qquad 2.36$$

$$R^{\cdot} + RO_2^{\cdot} \longrightarrow \text{Products} \qquad 2.37$$

$$RO_2^{\cdot} + RO_2^{\cdot} \longrightarrow \text{Products} \qquad 2.38$$

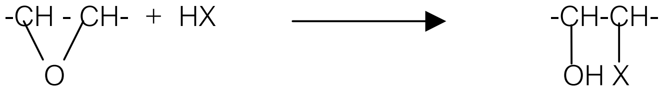
Figure 2.12 Simplified general scheme of polymer oxidation at low oxygen and medium oxygen partial pressures

In the case of polymers containing alkyl substituted double bond, e.g. polyisoprenes, the oxidation of polyene bond epoxidized to oxirane. This process is the epoxidation process, which is faster; however, in addition, there is a pronounced tendency for the highly strained epoxy ring to open. Such ring opening is also encouraged by presence of hydrogen ions and high reaction temperatures. Consequent to ring opening the following structures may be produced [10]:



2.39

The epoxidation process of polyene shown by Figure 2.13



2.40

Figure 2.13 The epoxidation process of polyene [11]

Certain important features of this system are to be noted:

1) The process is a chain reaction.
2) With each propagation cycle a molecules of hydroperoxide is formed and these become the main source of free radicals.
3) Termination may cause cross-linking or chain scission.

Polymer oxidation reactions generally show an induction period during which no visible changes occur in the material. However, after the induction period, the rate of oxidation increases rapidly: the first formed oxidation products accelerate the further degradation. The oxidation of polymers causes a deterioration of physical properties. Often, oxidation leads to decreased molecular weight and discoloration of the polymer. The oxidized polymers have lower mechanical strength. Oxidation also changes the electrical properties of polymers. In general, oxidized polymers have higher conductivity and a higher dielectric constant than non-oxidized materials. When the oxygen concentration is small, oxidation can cross-link the polymer. Such materials are in variably stiffer, more brittle, and less prone to creep than parent materials.

2.8 Effect of polymer properties on oxidation

1) The rate of diffusion of oxygen into the polymer and the solubility of gases are greater in amorphous regions than in crystalline domains. This implies that the rate of oxidation is greater in amorphous than in crystalline polymer [12].
2) The molecular weight may affect the oxidizability of polymers. The effect of molecular weight is different for oxidation of bulk polymers and polymer solutions. This may be explained by considering the rate of initiation and

termination: increasing molecular weight decreases the rate of initiation, but the rate of termination also decreases. The net effect is that the oxidizability is virtually independent of molecular weight [13].

3) The chemical structure of a polymer strongly affects its ability to resist oxidative degradation [14].

2.9 Literature survey

J. Hrivikova and A. blazkova (1980) studied the influence of relative molecular weight on rubber thermo–oxidation in air at $130\pm1^{\circ}$C [13]. In the range of low values of the internal viscosity up to 0.2 m^3/kg, the dependence induction period of carbonyl group to viscosity function has an exponential character as a consequence of the statistical character of chains breaking down during the degradation. It has been proved that the reciprocal value dependence of the mean viscosity molecular weight of unfractionated acetone–extracted natural rubber on the length of induction period is linear. The change in double–bond amount during the oxidation is not reflected in the induction period.

S. Tamura, K. Murakami and H. Kuwazoe (1983) studied the isothermal degradation of high cis–1,4–polyisoprene [15]. The degradation behavior of dicumyl peroxide–cure sample is similar to that of the uncrosslinked one. At the initial stages of degradation, weight loss in this sample is faster than that in an uncrosslinked one. A microstructural change in this polymer by thermal degradation is also very much larger than microstructural changes in the others.

K.K. Chee (1990) studied the kinetic study of random chain scission by viscometry [6] based on Saito's model for random chain scission, a novel procedure is developed to determine the activation energy of polymer degradation process. Basically, this is a simple viscometric technique which yields reliable results. It is superior to the existing viscometry which has been widely used to study the kinetic of random scission. The present method is successfully applied to the thermal degradation of natural rubber, polycarbonate, and poly(tetramethylene oxide) in bulk.

Flow properties of thermally depolymerized liquid natural rubber [16] were studied by N. Radhakrishnannair, N. M. claramma, N. M. Mathew, S. Thomas, and S. Someswara Rao. LNR samples were prepared by thermal depolymerization of natural rubber through the combined effect of mechanical, chemical, and thermal energies. High molecular weight samples, especially at lower temperatures, showed pseudoplastic behavior, whereas the low molecular weight samples were Newtonian at all temperatures. The viscosity of LNR considerably decreases with increase in temperature. The activation energy of flow was also calculated.

A viscometric method for determination of suitable induction period for polymers by thermal oxidation [17] was studied by J. F. Rodrigues and C.C. Bezerra (1996). Natural rubber films from Manihot glaziovii degradated at 90 °C were used as a model. A random chain scission process was applied. The resolution of the method is comparable to that of chemiluminescence and is superior to that of IR and DSC.

I.Nakamura and K. Fujimoto (1996) studied the development of new disposable catalyst for waste plastics treatment for high quality transportation fuel [18]. An iron supported coal–derived active carbon catalyst showed excellent activity for liquefaction of polypropylene at low reaction temperature (380 °C) to give colorless distillates selectively (98 wt. %) in the presence of small amount of H_2S.

J. Tangpakdee, M. Mizokoshi, A. Endo and Y. Tanaka (1998) studied the novel method for preparation of low molecular weight natural rubber latex [19]. Low molecular weight natural rubber (LNR) and LNR latex was prepared by oxidative degradation of deproteinized natural rubber (DPNR) latex in the presence of 1 phr of $K_2S_2O_8$ and 15 phr of propanal by shaking at 60 °C. The LNR latex is stable as the latex form and the dried rubber coagulated from latex is transparent and colorless. The LNR was a telechelic polymer containing aldehyde and ketone groups at both terminals as determined by NMR and molecular weight analyses.

The patent [20] of production process of depolymerized natural rubber (1999), described a production process of depolymerized natural rubber. It is possible to obtain depolymerized natural rubber in liquid form with narrow molecular weight distribution at high reaction efficiency. It is also possible to produce depolymerized natural rubber which is free from odor, coloring peculiar to natural rubber; and thus eliminate health hazard of allergenic reactions to proteins. The process according to the patent started from an addition of a carbonyl compound to natural rubber latex. The mixture was then subject to air oxidation in the presence of a radical forming agent. An alternative is to add a carbonyl compound to latex of deproteinized natural rubber and allow air oxidation in the presence of a radical forming agent.

Si–Dong Li, He–Ping Yu, Zheng Peng, Cheng–Shen Zhu and Pei–Sen Li studied thermal degradation of sol and gel of natural rubber in air at a constant heating rate [21]. The thermal degradation products of both sol and gel of natural rubber are hydroperoxide, carbonyl, and hydroxyl compounds. The formation of gel makes the temperature of the thermal degradation of natural rubber decreased and the rate of the thermal degradation increased.

CHAPTER 3

Materials and Experimental Methods

3.1 Materials

1. Concentrated latex (60% DRC) was from NY rubber.
2. Parafin oil C.G. (KAYDOL 350,101501) was from SR LAB. It was used as a heat transfer medium for rubber particles and to dissolve rubber particle [22] after water in latex evaporated.
3. Peroxide

   - Sodium perborate (96%) C.G. was from SOLVAY. Sodium perborate is soluble in water [23]. It dissolved in the aqueous phase of latex and initiated degradation of polyisoprene chain at decomposing temperature.

   - Sodium benzoyl peroxide A.R. (moistened with 25% H_2O) was from SR LAB. Sodium benzoyl peroxide is oil soluble peroxide. It dissolved in paraffin oil and initiated degradation of polyisoprene chains in oil phase.

4. Solvent
   - Acetone C.G. was from SR LAB.
   - Toluene C.G. was from SR LAB.
   - THF HPLC Grade was from LAB SCAN.
   - Chloroform NMR Grade

3.2 Apparatus

- Thermo-oxidative reactor, used for degradation of natural rubber at high temperature, was made from stainless steel equipped with electric heating device.

- Gel permeation chromatography (Water 510) was used for the determination of molecular weight averages and molecular weight distribution of degraded rubber.

- Fourier-transform infrared spectrophotometer (Perkin–Elmer, model 1760X) was used for the determination of functional groups of products from degradation.

- Brookfield Thermosel (TC 500) was used for the measurement of the viscosity of the degraded rubber.

- Proton Fourier–Transform Nuclear Magnetic Resonance 500 MHz (JNM.A 500) was used for the determination of functional groups of products from degradation.

- GG/MS (VG TRIO 2000) was used for identification of volatile product from degradation.

- Gas chromatography (Sim Dis Method) was used for the determination of boiling range distribution of degraded rubber.

3.3 Experimental Methods

Determination of dry rubber content [24]

10 g. of concentrated latex specimen was weighed and placed in a 100 ml beaker. Ten to twenty ml of water and fifteen to thirty ml of 6% v/v acetic acid in water were added into the concentrated latex for coagulation. After complete coagulation, the coagulated rubber was then dried in oven at $70 \pm 2\ ^{0}C$ until the coagulated rubber sheet was transparent. Weigh the dried coagulum and calculate DRC content.

<u>Calculation</u>

Calculated % DRC as follows :

% DRC =(W_d/W_l) x 100

where : W_d = weight of dry rubber

W_l = weight of concentrated latex specimen

Determination of optimum condition for degradation of natural rubber

Weigh accurately 25 g. of concentrated latex in a 250 ml beaker. Added 25 g. of paraffin oil into concentrated latex. Sodium perborate (calculated in phr. Unit) was added it into the mixture and stirred. Degradation was done at several time and temperature intervals.

The concentrated latex in this experiment had 60% DRC. From previous study, sodium perborate was dissolved in water phase and hydrolyzed in water to form hydrogen peroxide at 60–130 ^{0}C.

To study the effect of temperature on degradation, oil and concentrated latex was added together at several sodium perborate concentrations (0, 1.67, 3.33, 5 phr).

The degradation experiments were done at 150, 200, and 250 ^{0}C and at 2, 4, 6, and 8 hrs. The degraded rubber were extracted for 48 hr. with acetone and dried. Weighed the dried degraded rubber to determine volatile matters in degraded natural rubber.

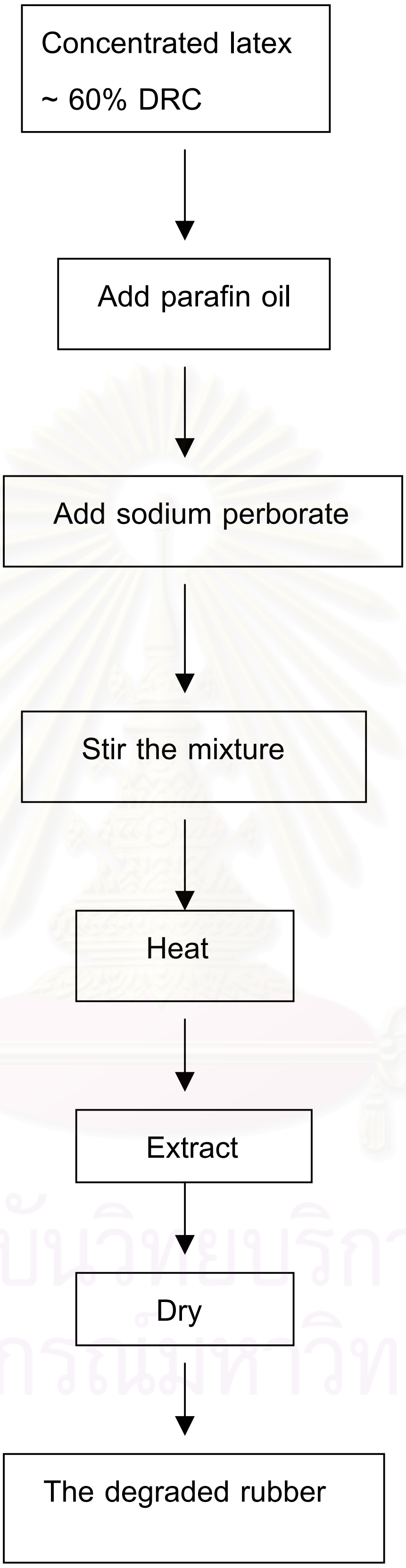


Figure 3.1: Schematic of natural rubber degradation process

To study how paraffin oil facilitated degradation, the degraded rubber from this condition was prepared in an open reactors. Weigh 25 g. of concentrated latex in a 250 ml beaker, add 10 g. paraffin oil, stirred the mixture until emulsified. The experiments were carried on at 0, 1.67, 3.33 and 5 phr. sodium perborate concentrations and at 150, 200, and 250 ^{0}C for 4 hrs. Afterward, acetone extractions were done for 48 h. and dried.

We compared 2 peroxides, Sodium perborate and benzoyle peroxide, upon the degradation of natural latex. Each peroxide was added into mixtures of paraffin oil and concentrated latex. at 0, 1.67, 3.33 and 5 phr. Experiments were conducted using 25 g. and 10 g.paraffin oil at 150, 200, and 250 ^{0}C for 4 hrs. The degraded rubber were extracted for 48 hrs. with acetone and dried.

The best condition (concentration of sodium perborate, temperature) is chosen from degradation data promoting the fastest time.

Degradation of concentration latex in the thermo–oxidative degraded reactor [3]

Concentrated latex was degraded at the selected conditions. Products from degradation are separated by distillation.

To produce degraded rubber weight 28 g. of concentrated latex and added 28 g. of parafin oil and 1.67 phr sodium perborate, stirred. Transferred the mixture in to the thermo–oxidative degraded reactor and heated at 350 ^{0}C for 4 hrs. After 4 hrs., the mixture was distilled and fractions of distillates were collected using normal distillation set.

Figure 3.2: Thermo-oxidative reactor.

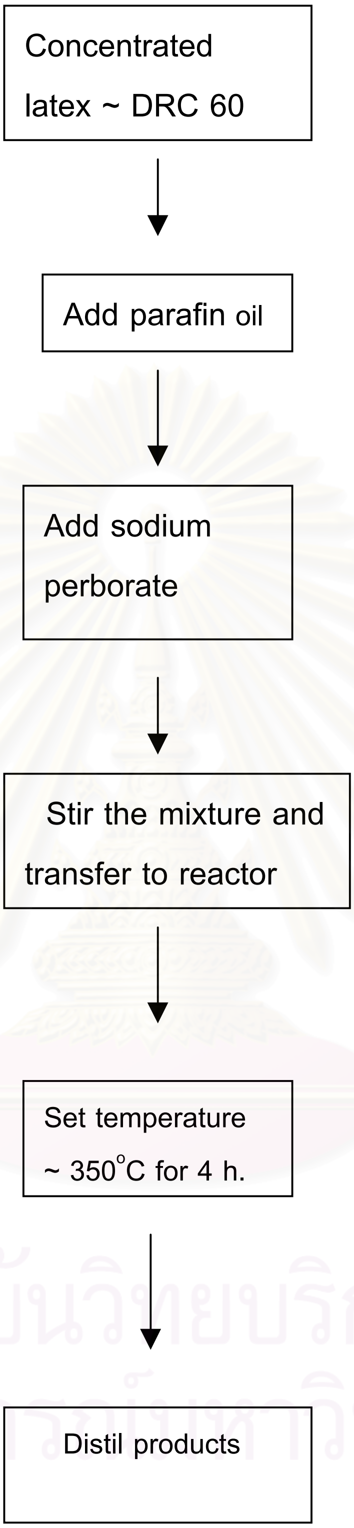


Figure 3.3: Schematic diagram of rubber degradation at high temperature.

Characteristic of Degraded rubber

Determination of molecular weight averages (Mw) and molecular weight distribution (MWD) by gel permeation chromatography [25]

Weigh accurately 0.01 g. of degraded rubber sample into a 20 ml vial with screw cap containing 10 ml of tetrahydrofuran (THF). After dissolution was complete, the solution was filtered through a membrane filter with pore sizes 5 µm before injection (100 µm) into a GPC system. The analyses were performed on a Water 510 with a series of 4 ultra styragel columns having nominal exclusion limits of 10^3, 10^4, 10^5 and 10^6 °A. The GPC conditions were: mobile phase-THF, flow rate 0.7 mlmin^{-1}, column temperature 35 °C, differential refractometer The Mw, Mn and polydispersity (Mw/Mn) were analyzed by the MAXIMA software for GPC by comparing with the standard calibration graph of Polystyrene Standard Mw ranging from 2.98×10^3 – 2.08×10^7.

Weight average or molecular weight (Mw) is related to the weight of the individual molecule as represented by the equation :

$$Mw = \Sigma(MiWi)/\Sigma Wi$$

where M = Mw of rubber in fraction i

W = Weight of the rubber in fraction i

and i = fraction number (from o to x)

Number average molecular weight (Mn) is dependent on the number of molecules having each discrete Mw and is represented by the equation.

$$Mn = \Sigma Wi/\Sigma Ni$$

where N = the number of molecules in fraction i

The Mw and Mn values may be used to provide an index for the range of molecular weight distribution as follows :

$$Mw/Mn = d$$

where d = polydispersity value

Determination of the functional groups of the degraded rubber

1. Fourier–Transform Infrared Spectrophotometer

The functional groups of the degraded rubber were investigated using Fourier–Transform Infrared Spectrophotometer (FTIR: Perkin–Elmer Infrared Spectrophotometer, model 1760X).

Weigh accurately 3.00 g. of degraded rubber sample into a 20 ml vial with screw cap containing 20 ml of toluene. After dissolution was complete, the solution was dropped on NaCl window. The NaCl window was dried by a heat gun, pressed and subjected to the FTIR analysis.

2. Fourier – Transform Nuclear Magnetic Resonance

The functional groups of the degraded rubber were characterized by nuclear magnetic resonance (Proton FT–NMR 500 MHz, JNM. A 500).

Weigh accurately 10.00 mg. f sample into a NMR tube containing 0.67 ml. of deuterium chloroform ($CDCl_3$). After dissolution was complete, the solution was analyzed by the FT–NMR.

Viscosity determination of degraded rubber by standard Brookfied Synchro–Lectric viscometer

Weigh accurately 3.00 g. of degraded rubber sample into a 20 ml screw cap vial containing 20 ml of toluene. Analysis was performed at 25 °C on a Brookfield viscometer equipped with number 18 spindle at 20, 50, 100, 180, 220 and 250 rpm.

Determination of the Boiling Range Distribution of degraded rubber by Gas Chromatography (ASTM D2887–93, Modified Method) [26]

Sample was dissolved with hexane before injection (100 μm). Analysis was performed on a GC equipped with HP–1 column (0.53 mm. O.D. x 10 m.) Run conditions were: initial column temperature 35 °C, final column temperature 350 °C, temperature ramp rate 10 °C/min, carrier gas helium, flow rate 12 ml/min, FID detector.

Determination of light distillated of degraded rubber by GC/MS

Weigh 10 mg. of light distillated of degraded rubber into a 10 ml screw cap vial containing 100 mg. of acetone, a mixture was injected into a GC/MS equipped with a DB–WAX column (0.25 mm. O.D. x60 m.). Run condition: initial column temperature 100 °C, final column temperature 220 °C, temperature ramp rate 7 °C/min, He carrier gas, flow rate 5 psi., photomultiplier detector, injection port temperature 220 °C.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Determination of molecular weight average of natural rubber

Molecular weight of natural rubber was determined, as well as paraffin oil, using GPC. The results are shown in Table 4.1. It can be seen that the molecular weight of natural rubber is 800 times that of paraffin oil. It is therefore necessary to degrade natural rubber to a low molecular weight liquid organics.

Table 4.1 Molecular weight average and polydispersity

No.	Sample	Mn	Mw	Polydispersity
1.	Natural rubber	2.94×10^5	1.64×10^6	5.57
2.	Paraffin Oil	1.95×10^3	2.05×10^3	1.05

4.2 Thermal degradation of natural rubber

4.2.1 Molecular weight reduction

To study the effect of temperature on degradation, a concentrated latex mixed with paraffin oil was heated at various temperature(150, 200, and 250^{o}C).Several samples were heated at different heating time i.e. 2, 4, 6, and 8 h.

After degradation, The molecular weight average and polydispersity of degraded rubber were determined using GPC. The results shown in Figure 4.1 and 4.2 indicate that molecular weight reduction depends on temperature and heating time. From Figure 4.1 degradation of NR proceeded gradually in the time, however the rate of degradation reduces somewhat heating time of 2 h.. The lowest Mw obtained is 3.02×10^4. For 150^{o}C, the Mw was reduced but increased again at about 6 h. suggested that at some temperature, the radicals formed may combine to become a larger molecule. Table A – 1 in Appendix A shows molecular weight averages and polydispersitys of degraded rubbers.

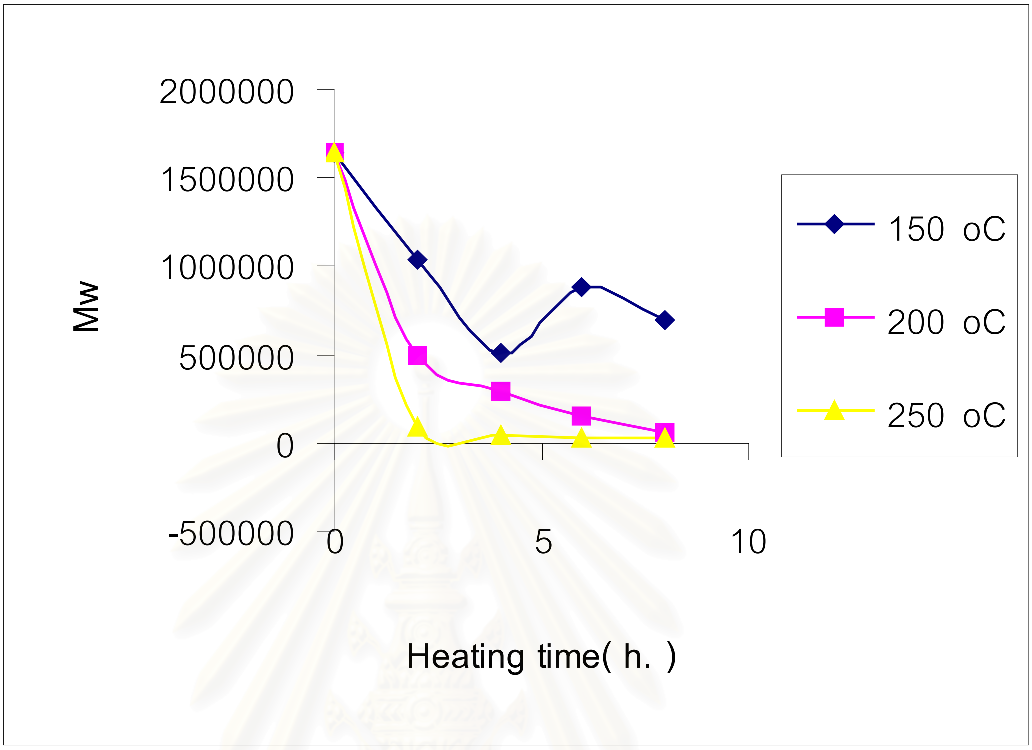


Figure 4.1 Molecular weight reduction with temperature and heating time

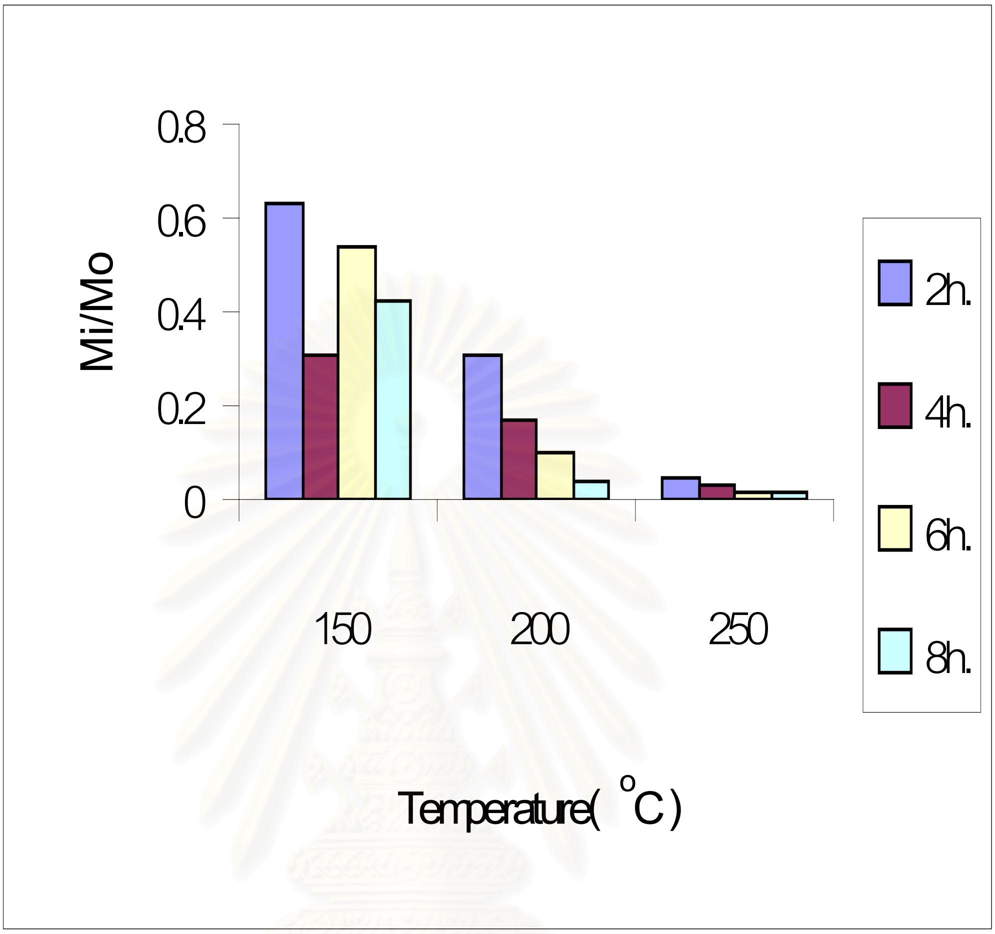


Figure 4.2 Molecular weight in fraction i (Mi) compared with initial value (Mo)

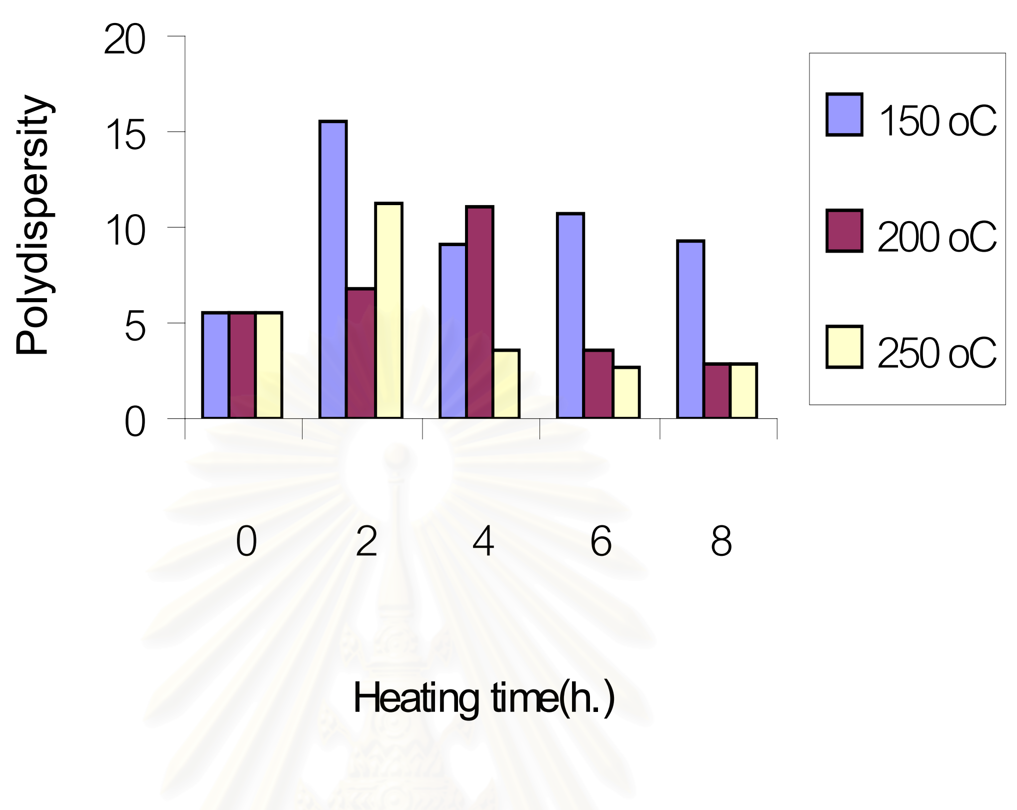


Figure 4.3 Polydispersity of degraded natural rubber

At 8 h., heating temperature ranging 150–250 °C (8 hr. is the final time of investigating time). As temperature increases, the molecular weight decreases and as heating time increases the molecular weight decreases too. After 2 hr. the molecular weight reduction is slower than 2 hr.. At 6 hr. and 8 hr., the molecular weight increase. This result shows at low heating temperature, that has a lot of nonstable radical chain and radical chain is big, so at low heating temperature the termination rate of nonstable radical chain is more rapid than at high heating rate.Figure 4.3 shows that polydispersity of degradation natural rubber at 200 and 250 °C, that has much lower than at 150 °C indicating uniform low molecular weight products.

4.2.2 Effect of temperature on the initial degradation rate

The initial degradation rate was determined by observation of the molecular weight reduction at 2 h. and compared with the reaction at other temperature. The rates from different temperature are shown in Table 4.2. It depends on temperature that increase when temperature increases.

Table 4.2 Initial degradation rate of degradation of natural rubber

Heating Temperature(°C)	Initial Rate($h.^{-1}$)
150 °C	$3.0\text{x}10^5$
200°C	$5.7\text{x}10^5$
250°C	$7.8\text{x}10^5$

4.2.3 Volatile matter and acetone extract

Volatile matter was determined as the weight loss during degradation of natural rubber (moisture excluded). Figure 4.4 shows percentage volatiles as a result of degradation. It can be seen that volatiles increase both with temperature and heating time indicating generation of small molecules from fragments of natural rubber. This behavior suggests that microstructural change in this sample occurs together with the production of volatile low molecular weight substrates. Large fragments having higher molecular weight will not be removed from the system during heating. At 150^{o}C % volatile is small indicating small fraction of natural rubber have been cracked.

Acetone extract indicates a quantity of low molecular weight polar compound remaining in the degraded rubber. Degraded rubber was extracted for 48 h. and the percentage extract determined as shown in Fig. 4.5. It shows a decreasing with temperature. It is pointed out that the molecular weight polar compounds evaporate as the temperature is increased. Table B in Appendix B shows percentage volatiles and acetone extracts.

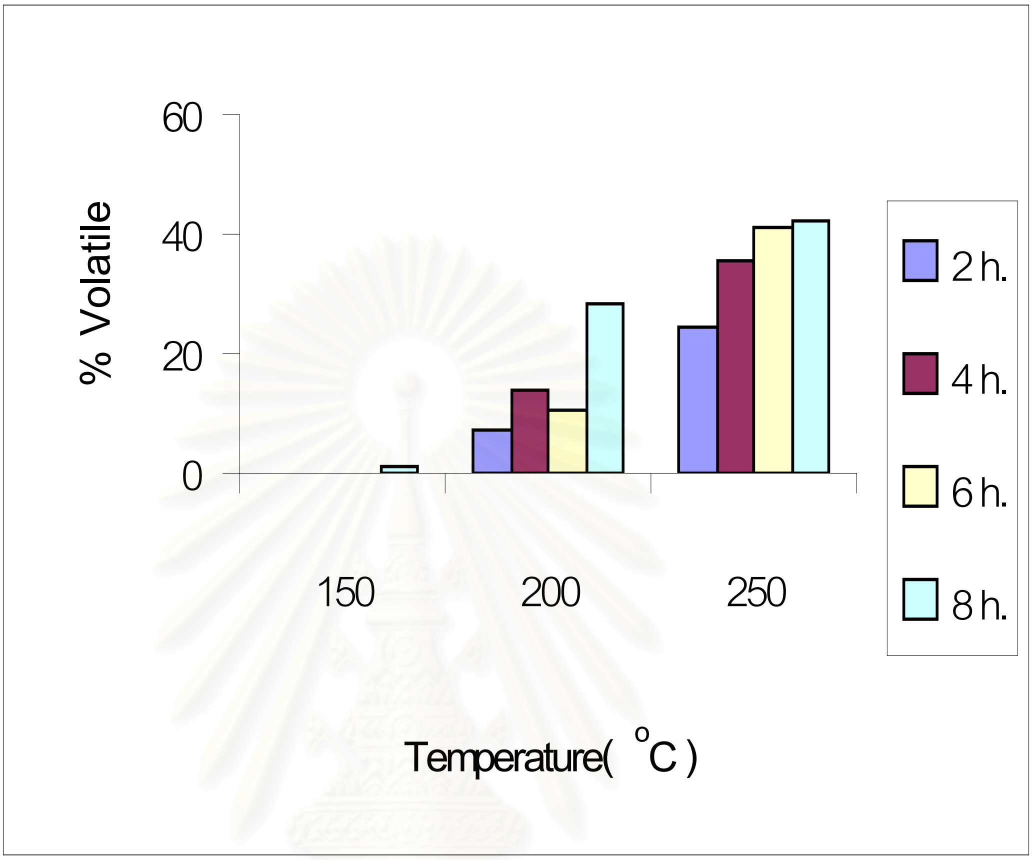


Figure 4.4 Volatile matter from degradation of natural rubber

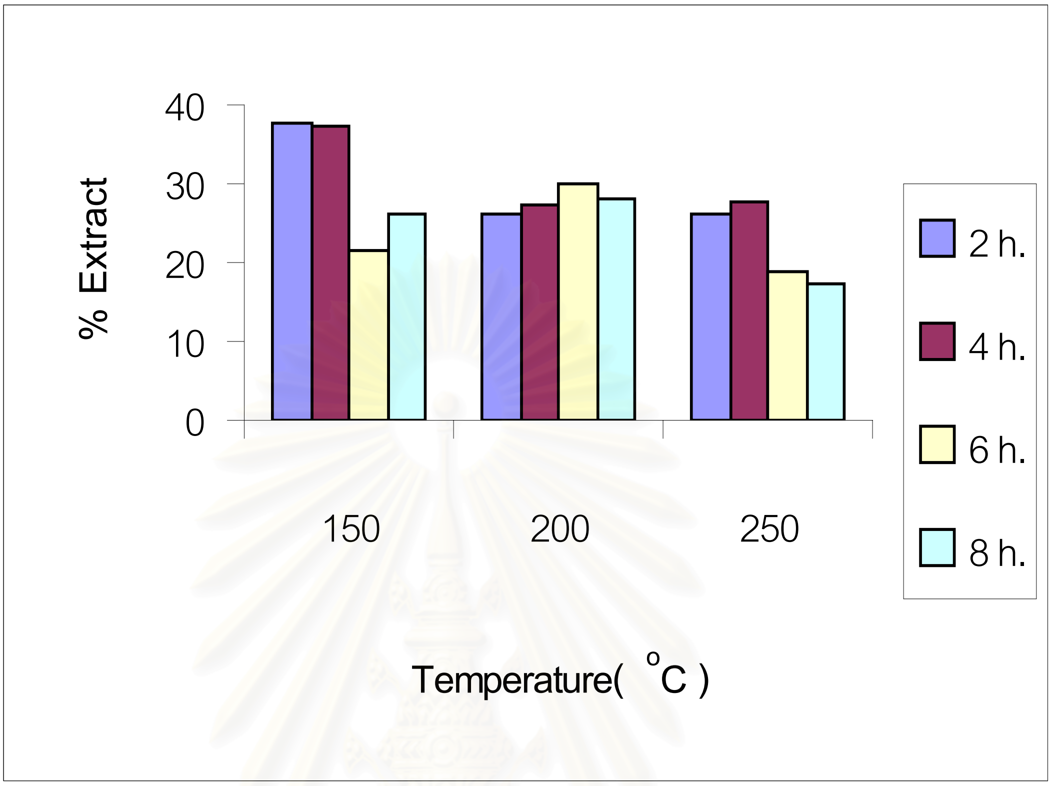
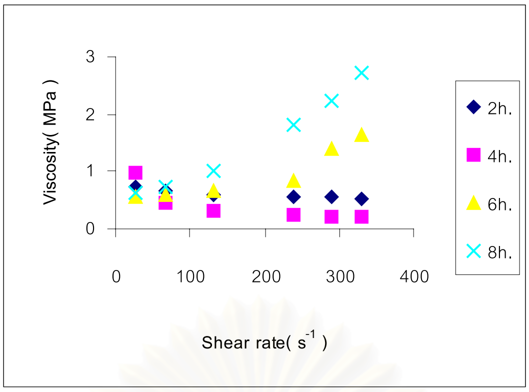


Figure 4.5 Percentage of acetone extract of degraded rubber

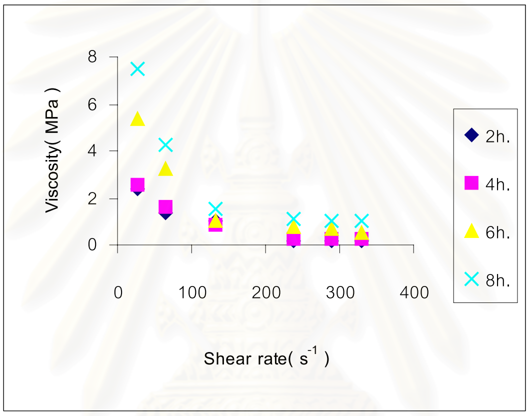
4.2.4 Viscosity of rubber degradation

The viscosity of degraded rubber was determined using Brookfield viscometer. The result shown in Fig. 4.6 indicates the viscosities of the degradation rubber solutions. Figure 4.6 shows the relation between viscosity with variations of shear rate at 25 °C. The viscosity curve of degradation of natural rubber shows that the degraded rubber is pseudoplastic liquid. Its viscosity decreases when shear rate increases. At low temperature of degradation, the decrease in viscosity on low heating heating time is slower than at high heating time and reflects characteristic of newtonian liquids. The degradation at 150 °C , the solution of degraded rubber is dilatant liquid when heating time increases. These result show at the low temperature the chain rubber is large and degradation is slow. The chain radicals were degraded and terminated so the product are not uniform. But at the high temperature the degradation rate is faster than the termination rate, the viscosities of degraded rubber solution are uniform. Table C in Appendix C shows the viscosity of degraded rubber solution.

a. 150 °C



b. 200 °C



c. 250 °C

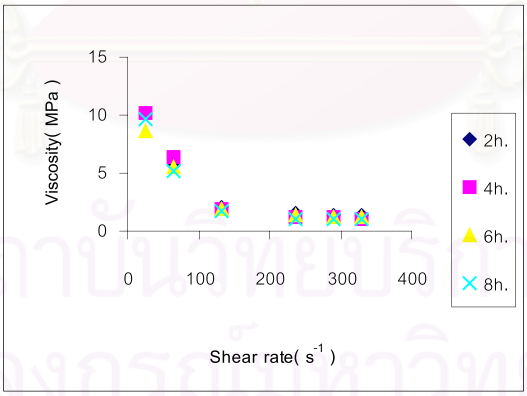


Figure 4.6 Viscosity of rubber degradation depends on temperature and heating time.

4.3 Degradation of NR with the aid of sodium perborate

4.3.1 Molecular weight reduction

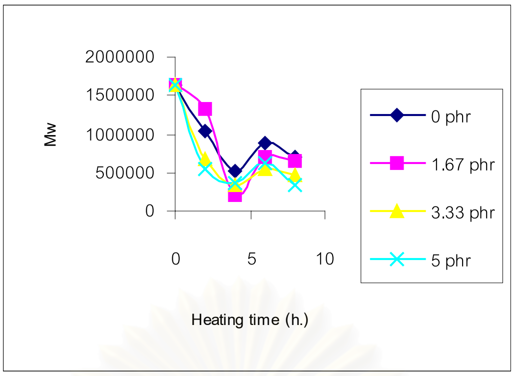
Degradation is enhanced by oxygen from the decomposition of peroxide, though peroxide may initiate crosslinking in the beginning. Transition metal such as boron is known to facilitate breaking up of double bonds. To study the effect of catalyst on degradation NR/paraffin mix was added with sodium perborate at different concentrations (0, 1.67, 3.33, 5 phr) for thermal degradation experiments.

After degradation, molecular weight average and polydispersity of degraded rubber were determined by GPC. Results are shown in Fig. 4.7 and 4.8. Molecular weight reduction appears not to depend on the cocentration of sodium perborate but on heating time. In Figure 4.7, for 150 ^{o}C the molecular weight decreases initially with heating time until about 4 h. the molecular weight increases and shows a peak. This result confirms the occurrence of termination with at least two degraded rubber molecules forming longer molecules.

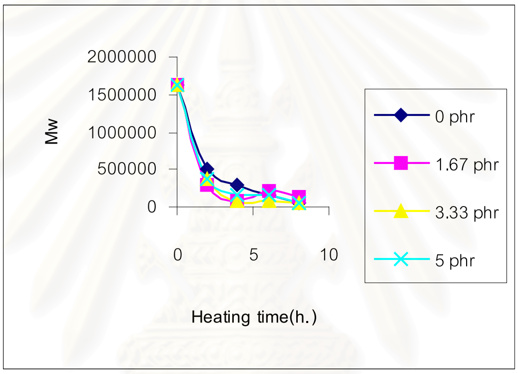
The molecular weight reduction does not depend on concentration of sodium perborate because when sodium perborate decomposes at 130^{o}C the oxygen is released and attack the rubber chain. The double bonds are broken or crosslinked between rubber chain. As a result polydispersity varies widely as shown in Fig. 4.9. However, it is more uniform at higher temperature when breaking of isoprene chain predominated.

It is further suggested that ionic liquid could be formed from fragments of degraded rubber and borates indicated by remain of decomposed carboxylic group in IR result (Table 4.9). The presence of ionic liquid influences the selective terminate of fracments, resulting in more uniform polydispersity. Table A–1 in Appendix A shows molecular weight averages and polydispersitys of degraded rubbers.

a. 150 °C



b. 200 °C



c. 250 °C

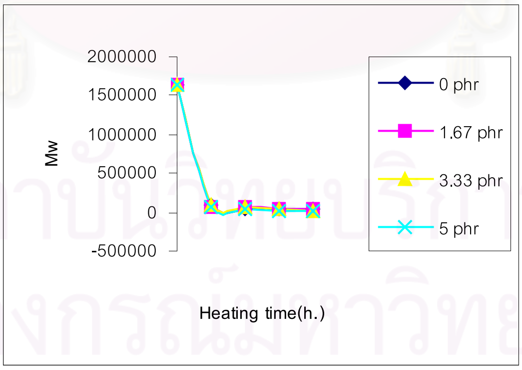
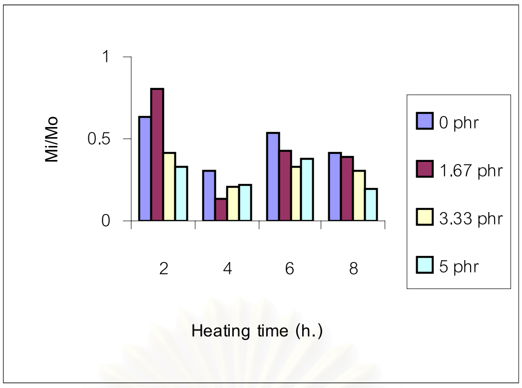
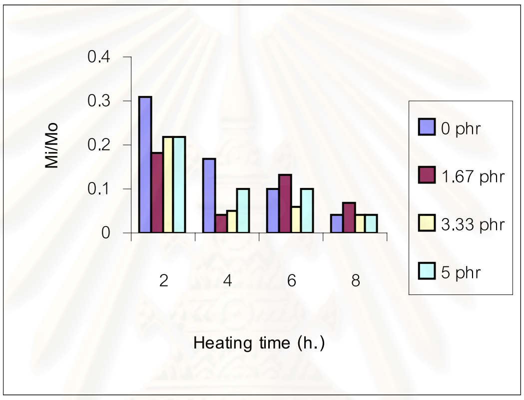


Figure 4.7 Dependce of molecular weight on concentration of sodium perborate

a. 150 °C



b. 200 °C



c.250 °C

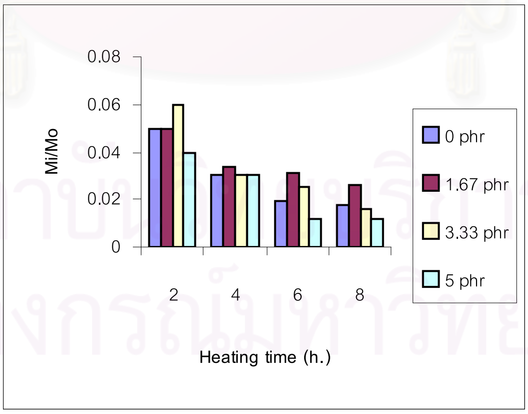
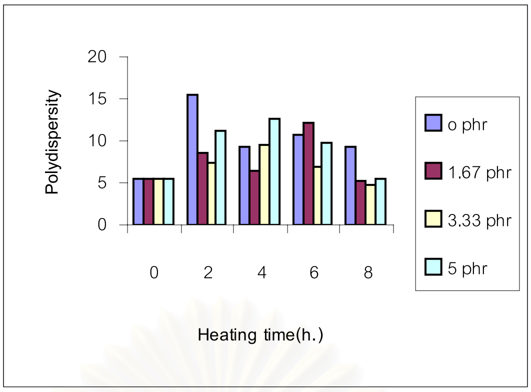
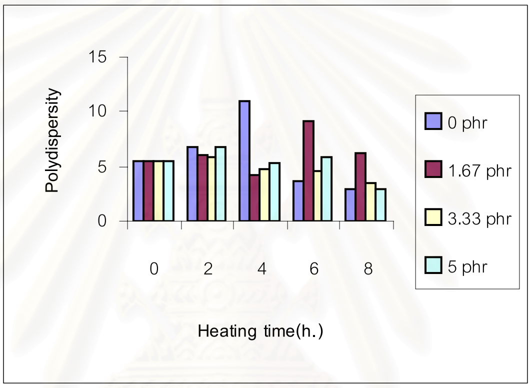


Figure 4.8 Dependence of molecular weight reduction on sodium perborate concentration

a. 150 ^{o}C



b. 200 ^{o}C



c.

c. 250 ^{o}C

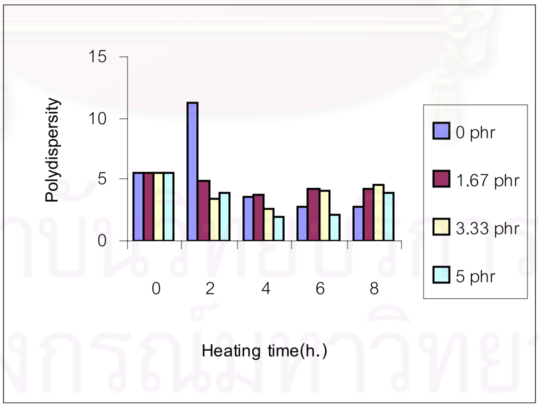


Figure 4.9 Influence of sodium perborate on polydispersity

4.3.2 Initial degradation rate of rubber degradation

The initial degradation rate was determined by observation of the molecular weight reduction at 2 hr..The degradation rates at several sodium perborate concentrations are compared. Table 4.3 shows dependence of the initial rate of degradation on concentration of sodium perborate

Table 4.3 Initial rate of rubber degradation

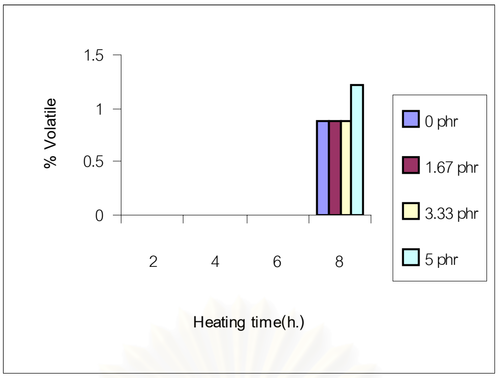
Temperature ^{O}C	Initial rate at different concentration of sodium perborate(h.$^{-1}$)		
	0 phr.	3.33 phr.	5 phr.
150	3.0 x 10^{5}	4.8 x 10^{5}	5.5 x 10^{5}
200	5.7 x 10^{5}	6.4 x 10^{5}	6.4 x 10^{5}
250	7.8 x 10^{5}	7.7 x 10^{5}	7.8 x 10^{5}

The rate of degradation increase with the concentration of sodium perborate

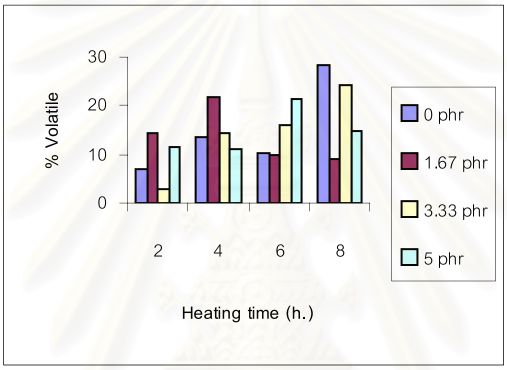
4.3.3 Volatile matters and acetone extract

Volatiles from degradation were determined by weight loss before and after degradation. Results shown in Figure 4.10, similar to thermal degradation, the volatiles increases with both temperature and time. However, the percentage is higher as a result of facilitation by sodium perborate. After degradation, the products were extracted for 48 h. with acetone. Percentage extract is shown in Figure 4.11. Concentration of sodium perborate has no notice all effects the percentage of extract. The polar compounds formed are generally about one-third original weight. Table B in Appendix B shows percentage volatile matter and acetone extract.

a. 150 °C



b. 200 °C



c. 250 °C

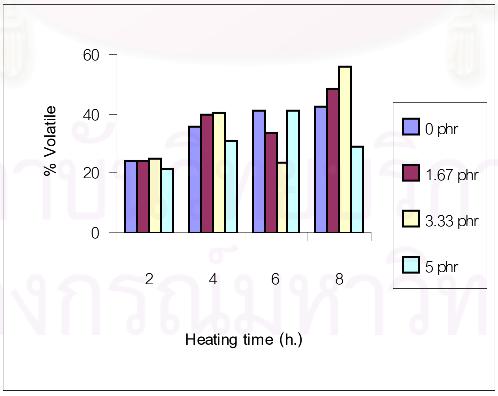
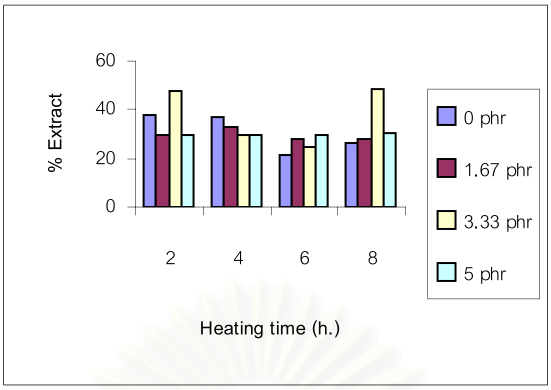
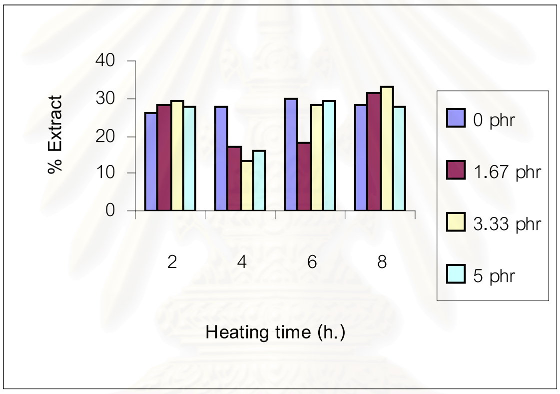


Figure 4.10 Facilitation of volatile generation by sodium perborate

a. 150 °C



b. 200 °C



c. 250 °C

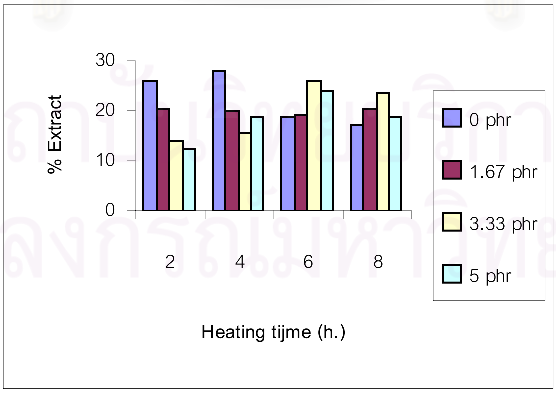
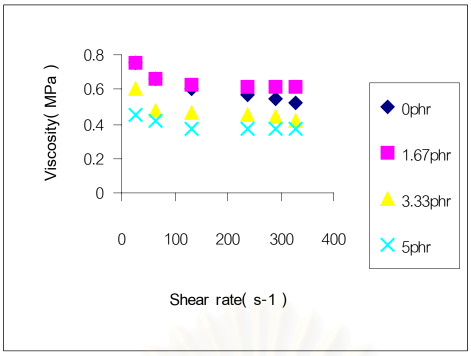


Figure 4.11 Acetone extract of rubber with sodium perborate facilitated degradation

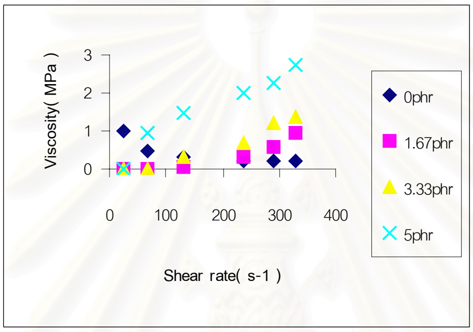
4.3.4 Viscosity of rubber degradation

The viscosity of degraded rubber was determined using Brookfield viscometer. Figures 4.12, 4.13 and 4.14 show the viscosity curve, that indicates the physical property of the degraded rubber solution similar to the thermal degradation. However the termination rates at low temperature and lower heating time are higher as a result of facilitation by sodium perborate. Table C in Appendix C shows viscosity of degraded rubber solution.

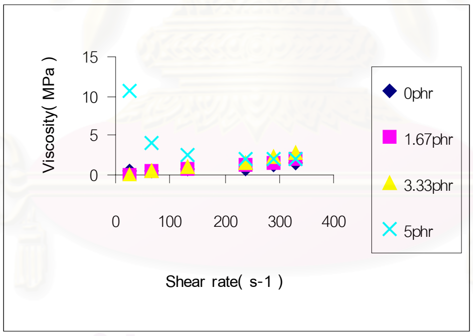
a. 2 h., 150 °C



b. 4 h., 150 °C



c. 6 h., 150 °C



d. 8 h., 150 °C

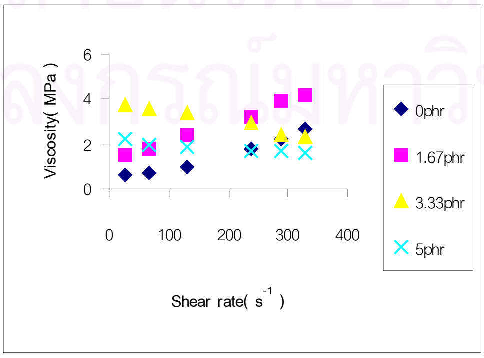
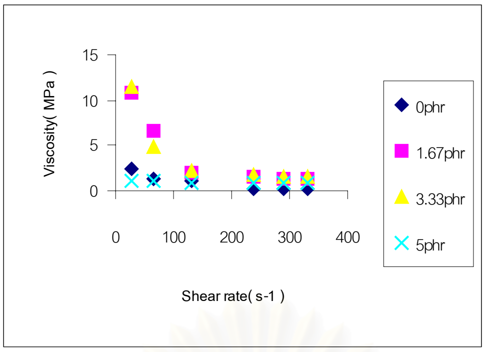
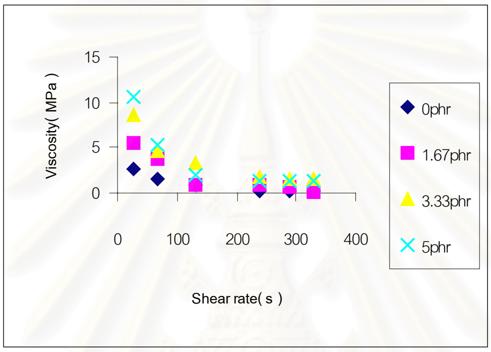


Figure 4.12 Influence of sodium perborate on viscosity of rubber degradation at 150 °C

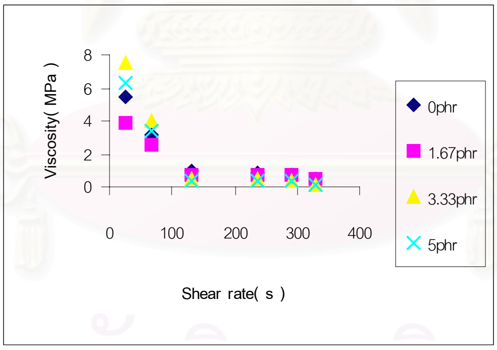
a. 2 h., 200 °C



b. 4 h., 200 °C



c. 6 h., 200 °C



d. 8 h., 200 °C

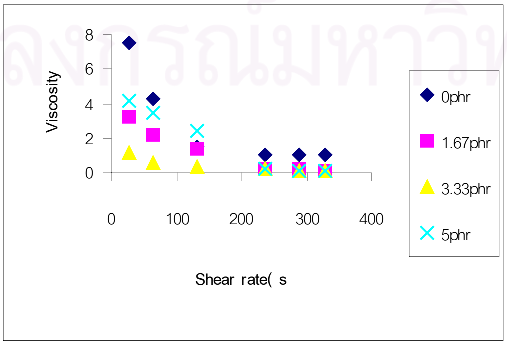
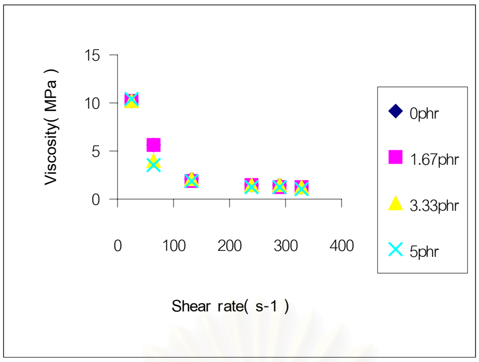
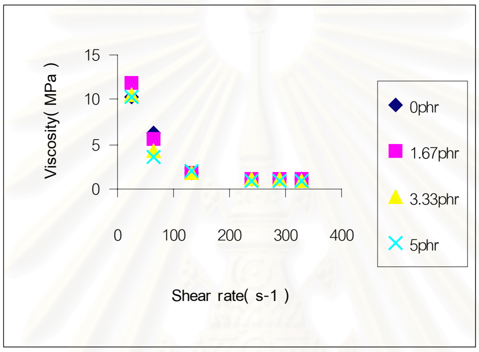


Figure 4.13 Influence of sodium perborate on viscosity of rubber degradation at 200 °C

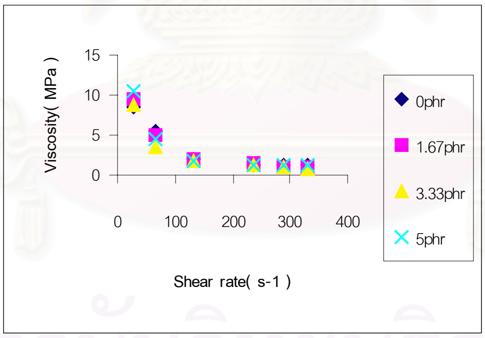
a. 2 h., 250 ^{o}C



b. 4 h., 250 ^{o}C



c. 6 h., 250 ^{o}C



d. 8 h., 250 ^{o}C

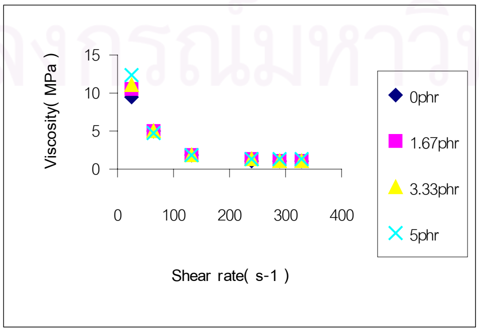


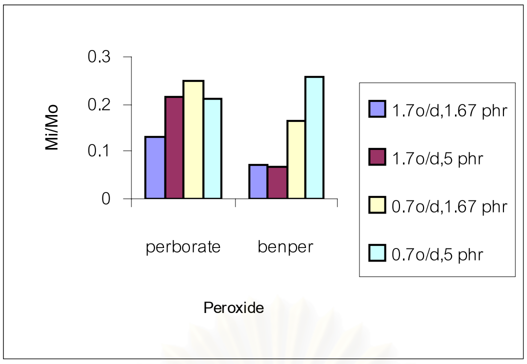
Figure 4.14 Influence of sodium perborate on viscosity of rubber degradation at 250 ^{o}C

4.4 Comparision of sodium perborate and benzoyl peroxide on rubber degradation

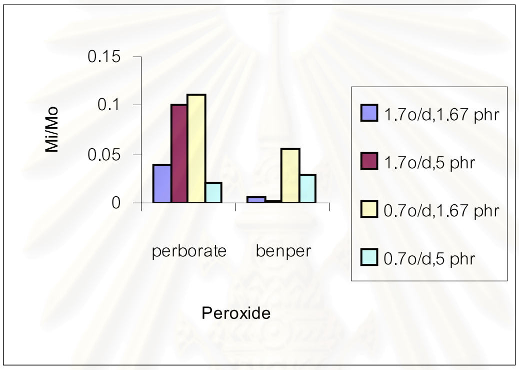
To study the facilitation of type of peroxide on degradation, sodium perborate and benzoyle peroxide were used in the degradation. The mixture of the paraffin oil and the concentrated latex was added the two type peroxide, with two peroxide concentrations(1.67, 5 phr), and two levels of paraffin oil(1.67 and 0.67 oil/DRC). Degradation was carried out at 150, 200, and 250^{o}C.

Figure 4.15 shows that molecular weight reduction depends on type of peroxide and quantity of paraffin oil. At high paraffin oil to natural rubber, benzoyl peroxide has greater fraction degradation than sodium perborate. At low paraffin oil to natural rubber, sodium perborate has greater effect than benzoyl peroxide. This is because benzoyl peroxide dissolves better in paraffin oil resulting in greater dispersion and decomposition of peroxide in rubber. Degradation due to oxygen is therefore prominent. On the other hand, when paraffin oil is low degradation due to temperature is more prominent. Table A – 2 in Appendix A shows molecular weight averages and polydispersitys of degraded rubber.

a. 150 °C



b. 200 °C



c. 250 °C

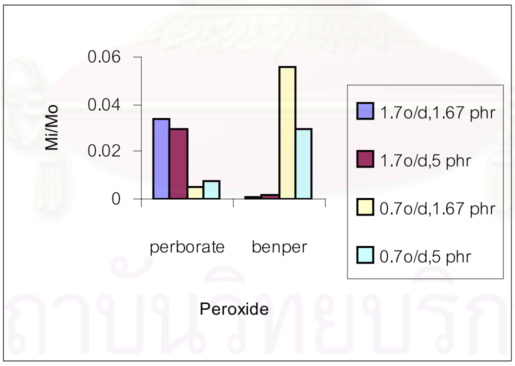


Figure 4.15 Comparision of type of peroxides on degradation of natural rubber ; o/d = paraffin oil/dry rubber contents

4.5 Thermo-oxidation of natural rubber at high temperature

The degradation of natural rubber in a stainless reactor was attempted by using 28 g of concentrated latex, added 28 g of paraffin oil. The mixture was added 1.67 phr of sodium perborate and mixed well. The mixture was loaded into the reactor. Temperature was set at 350 °C and thermo-oxidative degradation carried out for 4 h. was 79%. The product was brown liquid and the yield was 79% of original change under atmospheric pressure was collected as fractions shown in Table 4.4.

Table 4.4 Fraction from thermal-oxidative degradation of NR/paraffin oil

Temperature	% Distillate
120 – 180 °C	22
200 – 270 °C	6
> 270 °C	72
Total	100

Note: Boiling point of paraffin oil is 294 – 533°C

The result indicates a production of volatile at about 28%

4.5.1 Distribution of product from degraded rubber

The products from degradation in the reactor was tested for its boiling range by GC. The result is shown in Fig. 4.16 together with that of paraffin oil.

The fraction (b.p. < 294 °C) is 24 % and a large boiling point range compounds. For the removing fraction the boiling range as narrows indicating close molecular weight product. Table D in Appendix D shows boiling range of paraffin oil and degraded rubber.

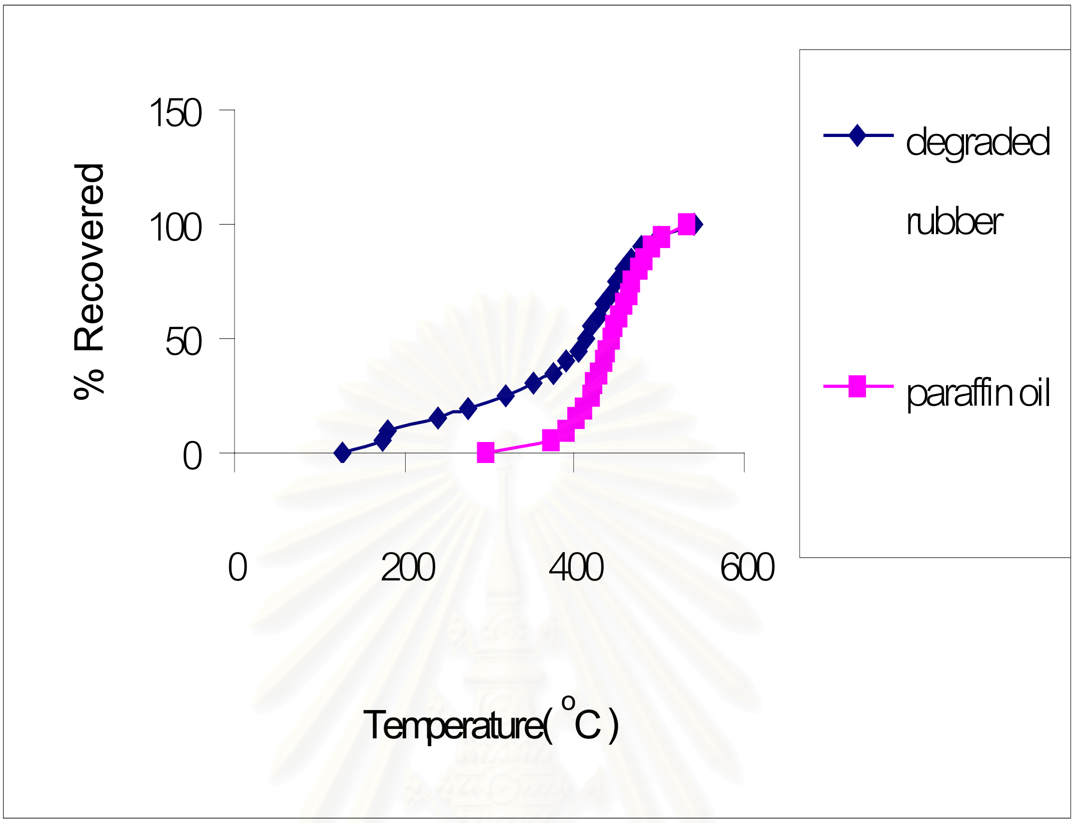


Figure 4.16 Boiling range distribution of degraded rubber and paraffin oil

4.5.2 Identification of functional groups of light fraction

The functional groups of compounds from degradation at high temperature (350^{o}C) were determined using FT-IR. The IR spectrum of the light distillate of degraded rubber (bp. 120–180 ^{o}C) on NaCl cell were recorded on using Perkin Elmer FT–IR spectrometer 1760. IR spectrum is shown in Fig. 4.17. The assignments of the important peaks are shown in Table 4.7

Table 4.5 Important peaks of the light distillate fraction

Wave Number, cm.$^{-1}$	Peak Assignment
3078	C-H stretching of Cyclopropane
2919	C-H bending CH_3 and CH_2
1721	C=O stretching of ester
1644	-C=C- stretching of alkene
1415,1378	C-H stretching of CH_3 and CH_2
1250	C-O-C stretching of epoxide
1240	C-O stretching of acetate
1153	C-O stretching and O-H deformation of 3^{o} alcohol
	$RCH=CH_2$
968	Trans epoxide
897	CH_2 rocking of C-$(CH_2)_n$-C ; n = 2
758	CH_2 rocking of C-$(CH_2)_n$-C ; n = 4
723	

The functinal groups of light distillate of degraded rubber are epoxide, ester, alkene and alcohol.

The functional groups of medium distillate of degraded rubber (200–270 ^{o}C) were identified by FT–IR, The result shown in Figure 4.18 and the assignments of important peaks are listed in Table 4.8

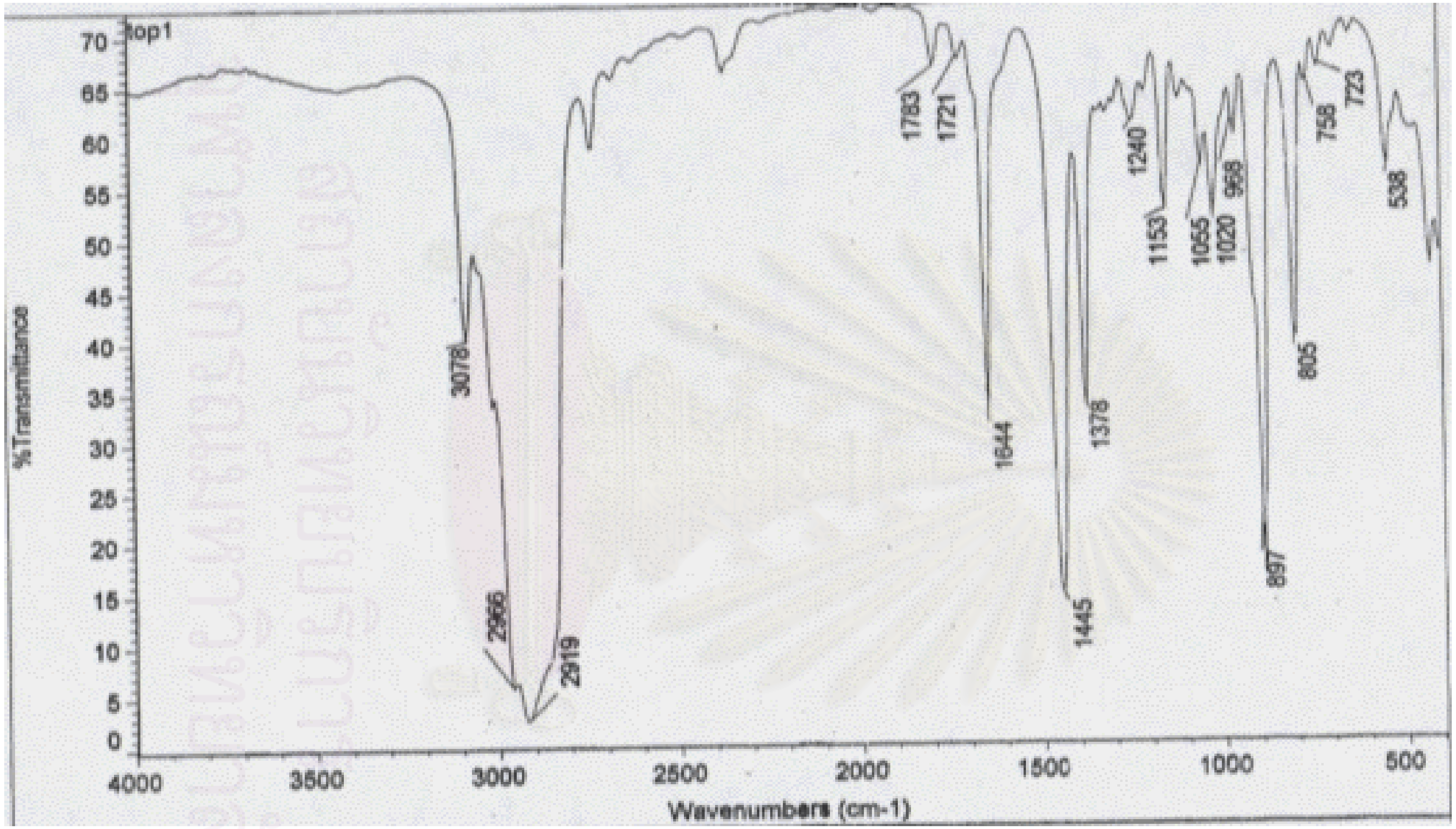


Figure 4.17 IR spectrum of the light distillate fraction

Table 4.6 Important peaks of the medium distillate fraction (200–270 °C)

Wave Number, cm	Peak Assignment
3442	O-H stretching of polymeric alcohol
2919	C-H stretching of CH3 and CH2
1644	-C=C- stretching of alkene
1465, 1378	C-H stetching CH3 and CH2
897	C-H deformation of R1R2C=CH2

The functional groups of medium distillate are alkene and alcohol.

The FT-IR spectrum of heavy distillate of degraded rubber(> 270 °C) is shown in Figure 4.19 Shows that IR spectrum. The assignments of the important peaks are listed in Table 4.9

Table 4.7 Important peaks of the bottom of degraded rubber (>270°C)

Wave Number, $cm.^{-1}$	Peak Assignment
3437	O-H stretching of polymeric alcohol
2919	C-H stretching of CH_3,CH_2
1650	-C=C- stretching of alkene
1450,1378	-C-H stretching of CH_3 and CH_2
1158	C-O stretching, -O-H deformation of 3^oalcohol

The functional groups of heavy distillate of degraded rubber are alkane, alkene and alcohol. Figure 4.20 shows NMR spectrum of heavy distillate, that exhibited two chemical shifts of protons, that shows in Table 4.10

Table 4.8 Chemical shifts of protons from NMR spectrum of heavy distillate

Chemical shifts of proton	Peak Assignment
1.25	CH_3, CH_2
0.85	CH_2

From ^{1}H-NMR spectrum, the heavy distillate is alkene and alkane from changing molecular structure of polyisoprene.

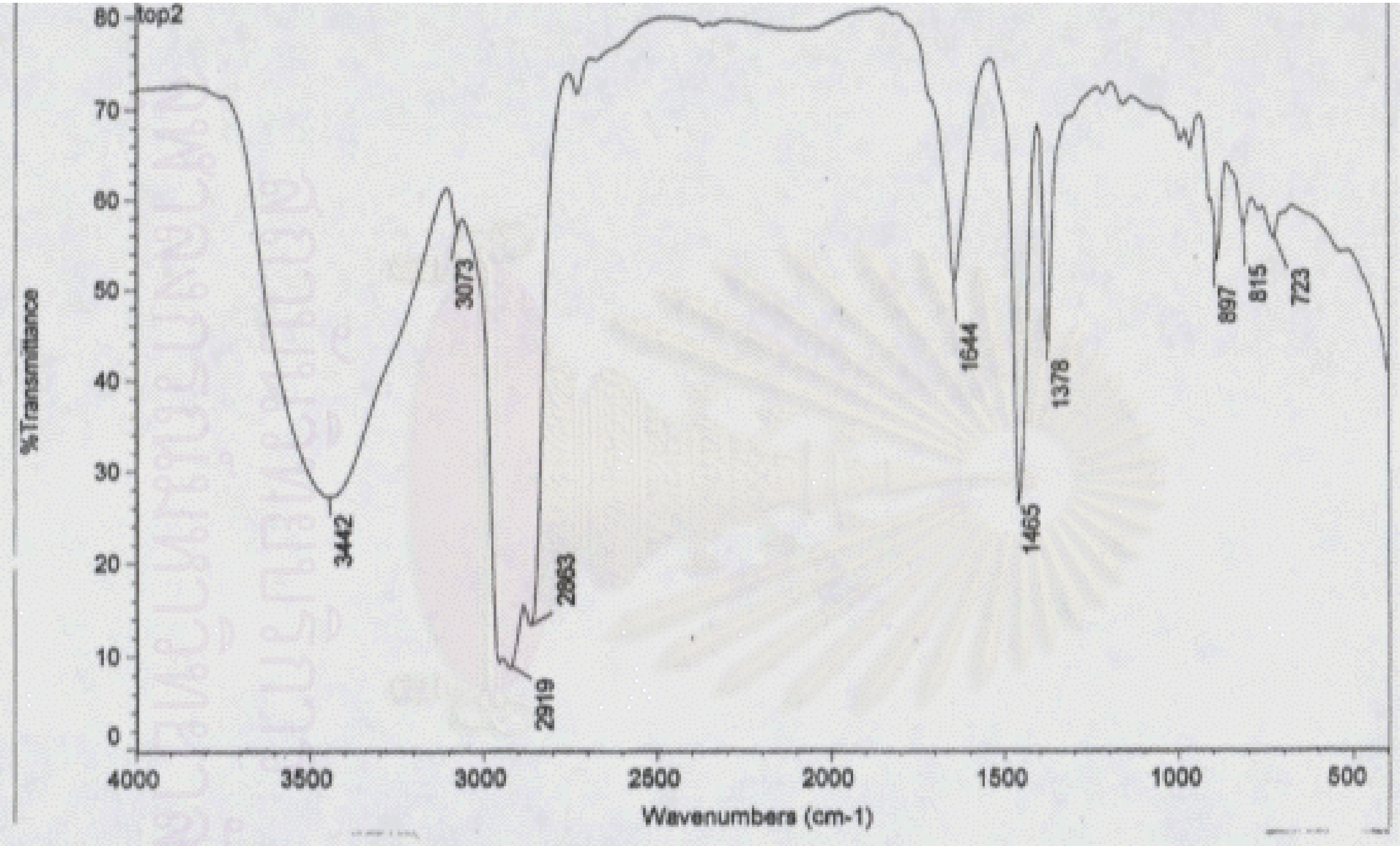


Figure 4.18 IR spectum of the medium distillate fraction

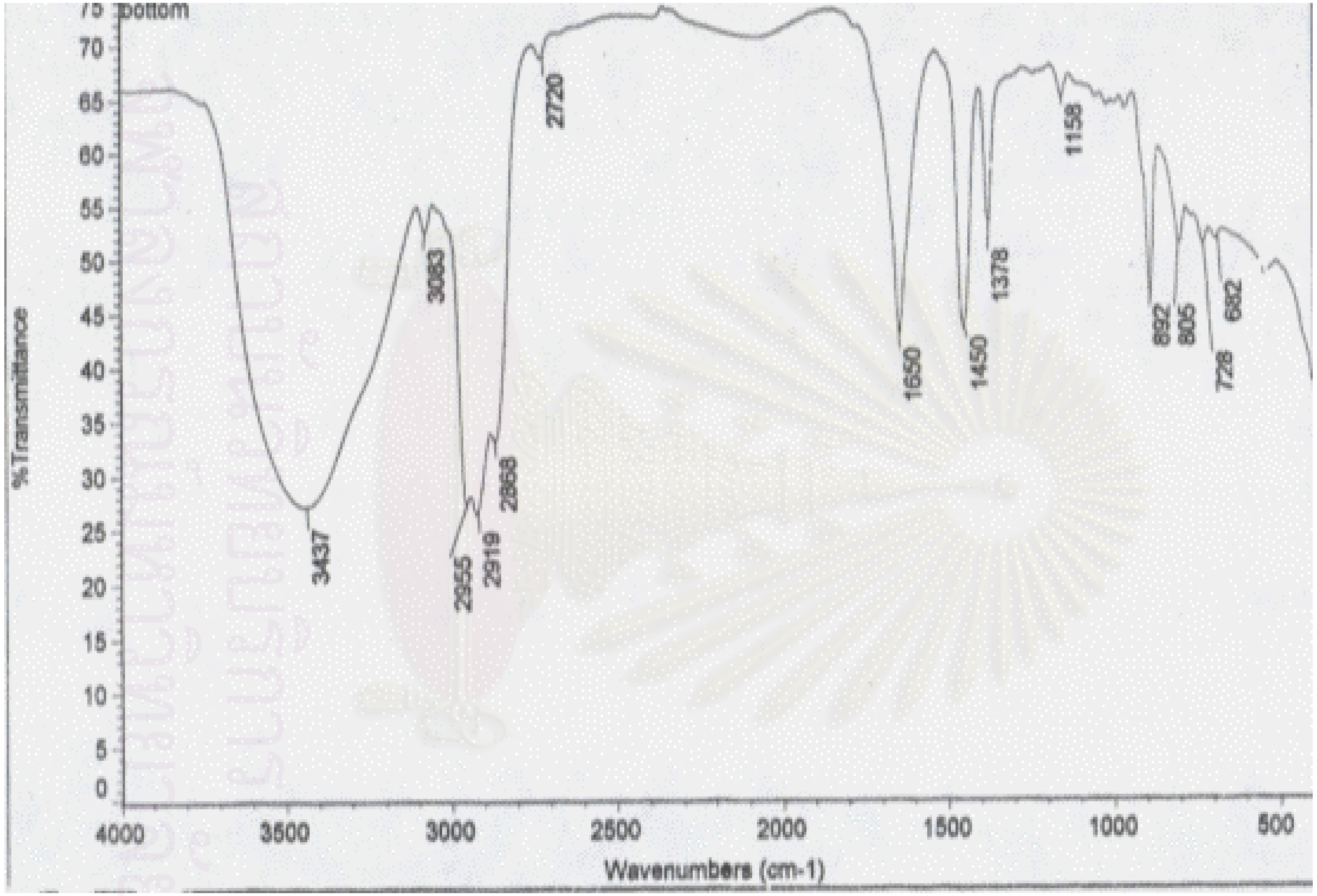


Figure 4.19 IR spectrum of the heavy distillate fraction

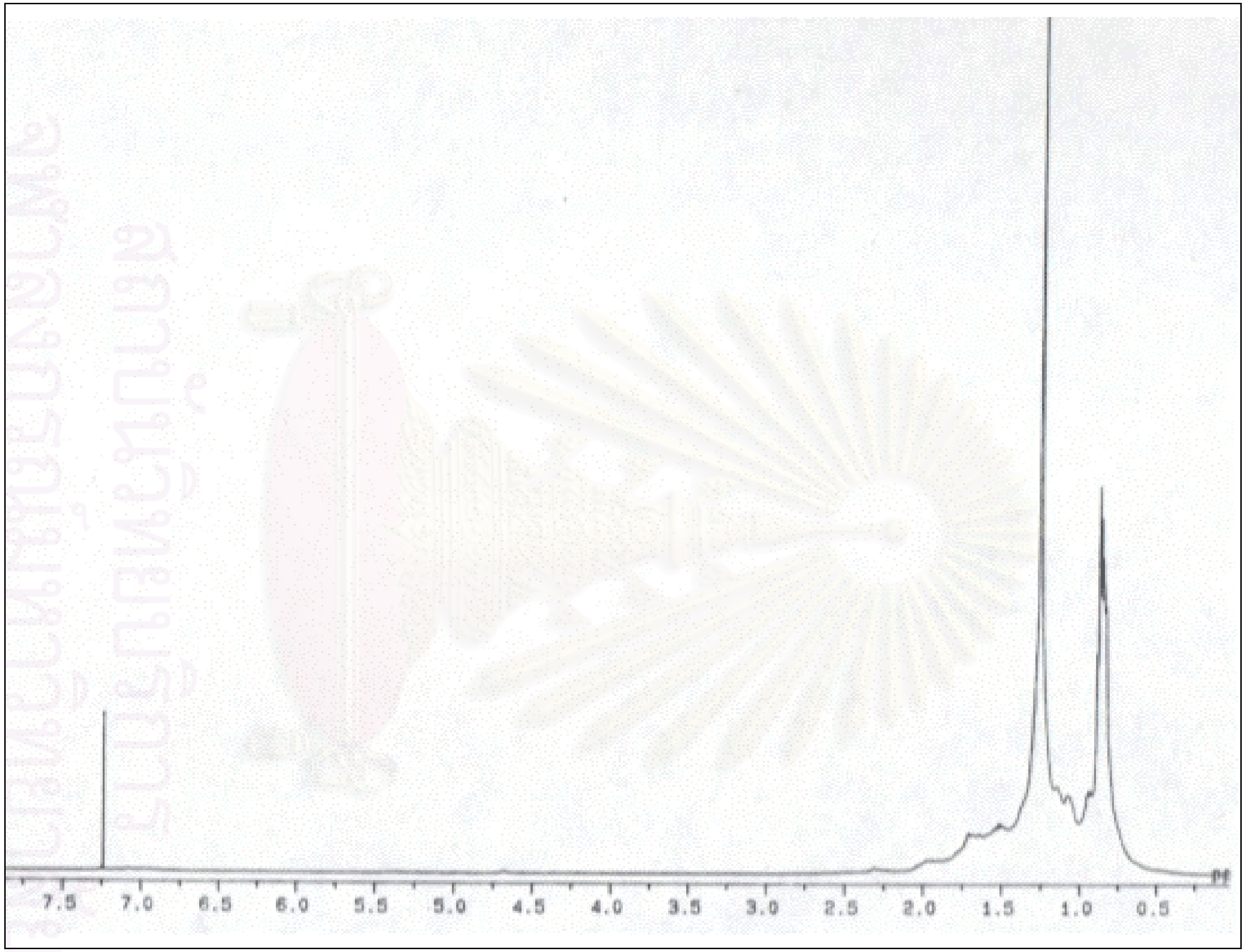


Figure 4.20 TheH^1-NMR spectum of heavy distillate

4.5.3 Identification of light distillate by GC-MS

GC-MS was used to identifie the light distillate. Sample was dissolved by hexane and injected into DB-WAX column. The chromatogram of the light distillate is shown in Fig. 4.21. Retention time of sample is 17.36 min.. The other peaks are solvent and impurity in solvent.

MS-spectrum of the distillate is shown in Fig. 4.22. The compounds of the distillate which identified by GC/MS are listed in Table 4.11. From MS-spectrum, the light distillate of degraded rubber consists of 1,3–p–menthadiene or alpha–terpinene or limonene. but the GC has only one peak. This result shows that light distillate of degraded rubber has Isomer compounds which cannot be separated by gas chromatography.

Table 4.9 The compounds of the distillate which identified by GC/MS

Stucture of compound	No.	Compound name	Formula	Molecular weight
	1	1,3–p–menthadiene	$C_{10}H_{16}$	136
	2	Alpha–terpinene	$C_{10}H_{16}$	136
	3	Terpinolene	$C_{10}H_{16}$	136
	4	Beta–terpinene	$C_{10}H_{16}$	136
	5	Alpha–pyronene	$C_{10}H_{16}$	136
	6	Limonene	$C_{10}H_{16}$	136
	7	Beta–phellandrene	$C_{10}H_{16}$	136
	8	Sabinene	$C_{10}H_{16}$	136
	9	Alpha–terpinene	$C_{10}H_{16}$	136
	10	3-carene	$C_{10}H_{16}$	136

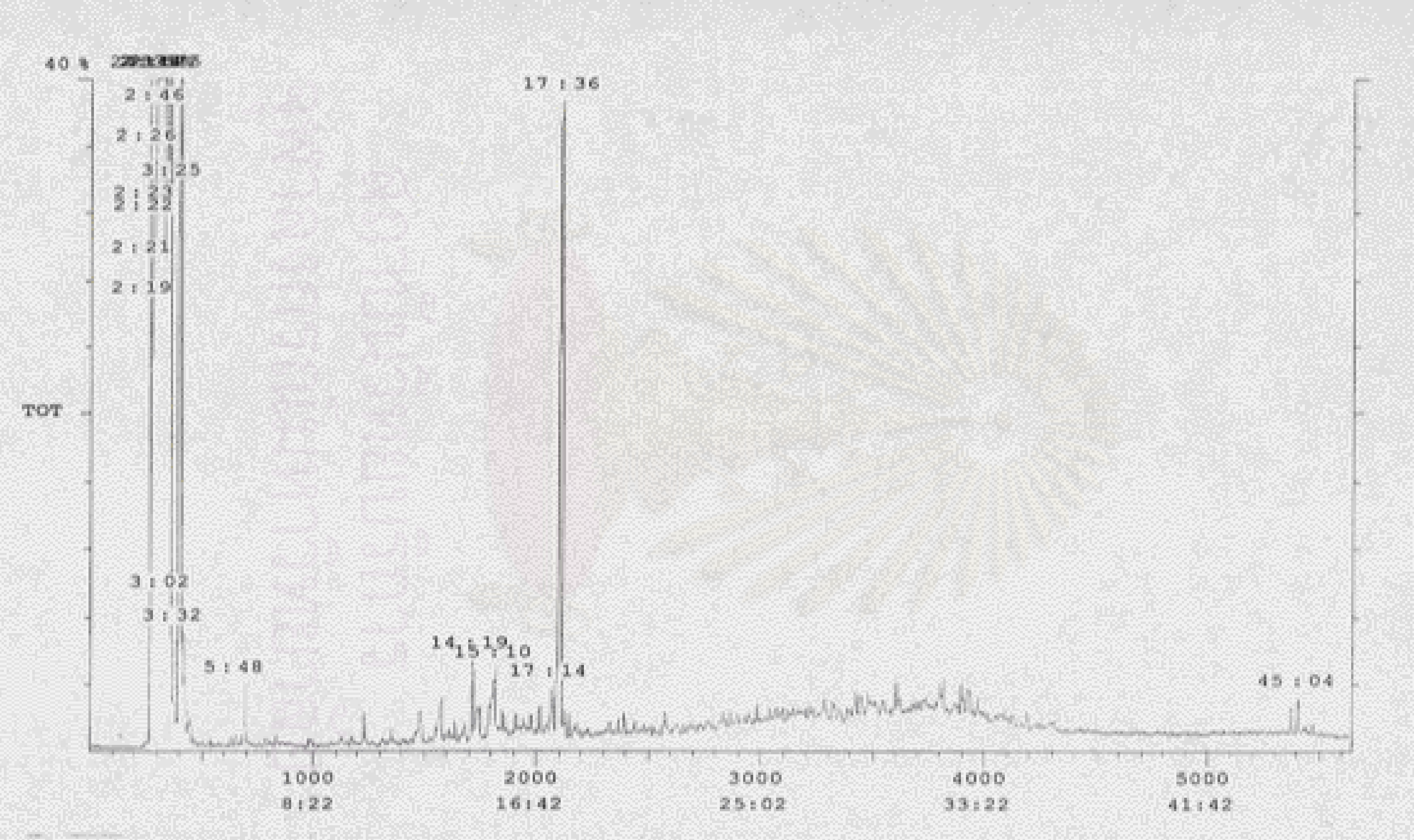


Figure 4.21 The GC chromatogram of light distillate(b.p. 120-270 °C)

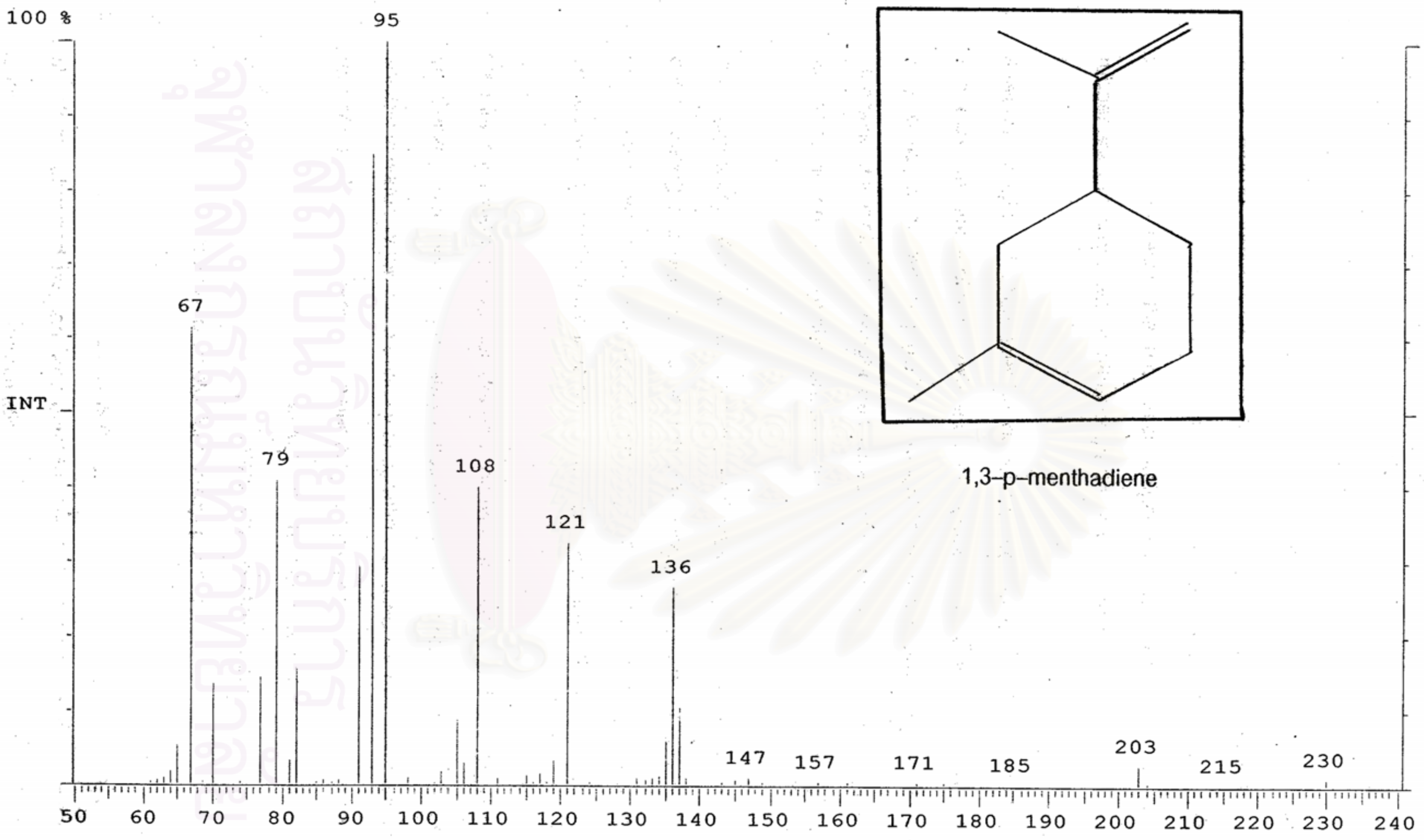


Figure 4.22 The MS spectrum of light distillate (b.p. 120-270 °C)

CHAPTER 5

CONCLUTIONS

1. Molecular weight reduction depends on heating temperature and heating time. When heating temperature increases the molecular weight decreases, when heating time increases the molecular weight decreases. In certain conditions when heating time increase the molecular weight increases because the degraded rubber are terminated with another degraded rubber chains.

2. Molecular weight reduction does not depend on concentration of sodium perborate. The experimental indicates existence of competition between curing rate and degradation of rubber. The molecular weight increases when curing predominates, otherwise the molecular weight decreases. It is difficult to control the molecular weight reduction by thermal-oxidation process.

3. Initial degradation rate (at 2 hrs. heating time) depends on heating temperature and concentrating of sodium perborate. When heating temperature increases the initial degradation rate increases. At 2 hrs. heating time, the degrading rate dominates and competition between curing and degrading rates are difficult to control.

4. The molecular weight reduction depends on type of catalyst and quantity of paraffin oil. Benzoyl peroxide is the catalyst soluble in oil whereas sodium perborate is soluble in water. When more quantity of paraffin was used the molecular weight was reduced by benzoyl peroxide greater than sodium perborate. When the quantity of paraffin oil decreases, molecular weight was reduced by benzoyl peroxide lower than can be reduced by sodium perborate. The paraffin oil acts as antioxidant for sodium perborate but is a promotor for benzoyl peroxide.

5. The degradation of natural rubber is random scission. Upon degradation, chemical structures changed by heat and catalyst. The light distillate of degraded rubber changes structure to 1,3-p-menthadiene and its isomers.

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APPENDIX A

DETERMINATION OF MOLECULAR WEIGHT OF DEGRADED RUBBER

Molecular weight average and polydispersity of natural rubber degraded using sodium perborate at 1.7 o/d are shown in Table A – 1 (o/d = paraffin oil/dry rubber content).

Table A – 1 Molecular weight average and polydispersity of degraded rubber (1.7 O/D)

Temperature and heating time	Sample No.	Concentration of sodium perborate, phr	Mn	Mw	Polydispersity
150°C 2 h.	1	0	66732	1036712	15.5
	2	1.67	156150	1333605	8.54
	3	3.33	90855	672316	7.39
	4	5.00	49026	545061	11.1
150°C 4 h.	5	0	55545	509320	9.16
	6	1.68	33061	214275	6.48
	7	3.34	35972	344218	9.56
	8	5.00	49039	617128	12.6
150°C 6 h.	9	0	42811	455460	10.6
	10	1.69	58010	709426	12.2
	11	3.35	122499	852705	6.96
	12	5.00	82339	798279	9.69
150°C 8 h.	13	0	74127	693770	9.35
	14	1.70	121834	645597	5.29
	15	3.36	100804	473826	4.70
	16	5.00	60727	335537	5.52
200°C 2 h.	17	0	73101	499853	6.83
	18	1.71	48331	288847	5.97
	19	3.37	61887	366173	5.91
	20	5.00	54811	368352	6.72

Table A – 1 (continued)

Temperature and heating time	Sample No.	Concentration of sodium perborate, phr	Mn	Mw	Polydispersity
200°C	21	0	26101	288234	11.0
4 h.	22	1.72	17012	72219	4.24
	23	3.38	17790	83571	4.69
	24	5.00	31656	169119	5.34
200°C	25	0	43885	158138	3.60
6 h.	26	1.73	51507	466931	9.06
	27	3.39	18210	84500	4.64
	28	5.00	17797	104470	5.87
200°C	29	0	21299	60744	2.85
8 h.	30	1.74	19593	122318	6.24
	31	3.40	17106	59562	3.48
	32	5.00	20254	60307	2.97
250°C	33	0	28315	85124	11.3
2 h.	34	1.75	14868	73821	4.96
	35	3.41	26051	90916	3.48
	36	5.00	84506	73542	3.92
250°C	37	0	12513	44667	3.57
4 h.	38	1.76	11081	42207	3.81
	39	3.42	10170	26097	2.57
	40	5.00	10252	19773	1.93
250°C	41	0	11824	32306	2.73
6 h.	42	1.77	13116	55006	4.19
	43	3.43	13488	41224	4.05
	44	5.00	9209	20062	2.17

Table A – 1 (continued)

Temperature and heating time	Sample No.	Concentration of sodium perborate, phr	Mn	Mw	Polydispersity
250°C 8 h.	45	0	14004	30190	2.79
	46	1.78	12177	50848	4.17
	47	3.44	12214	55361	4.53
	48	5.00	10438	41133	3.94

Molecular weight average of natural rubber degraded using sodium perborate and benzoyl peroxide at 1.7, 0.67 o/d are shown in Table A – 2.

Table A – 2 Molecular weight average of natural rubber degraded using sodium perborate and benzoyl peroxide (heating time 4 h.).

Temperature	Concentration of peroxide Phr	Benzoyl peroxide		Sodium perborate	
		1.67 o/d	0.67 o/d	1.67 o/d	0.67 o/d
150 °C	1.67	116131	268578	214275	39896
	5.00	111368	421746	617128	24855
200 °C	1.67	9229	58066	72219	13910
	5.00	20474	193394	169119	9295
250 °C	1.67	1803	91274	42207	5823
	5.00	2563	48532	19773	6675

APPENDIX B

DETERMINATION OF VOLATILE MATTER AND ACETONE EXTRACT

Percentage volatile matter and acetone extract are shown in Table B-1.

Table B-1 Percentage volatile matter and acetone extract

Temperature and heating time	Sample No.	Concentration of sodium perborate, phr	% Volatile matter	% Extract
150 °C 2 h.	1	0	0	37.8
	2	1.67	0	29.7
	3	3.33	0	48.0
	4	5.00	0	29.3
150 °C 4 h.	5	0	0	37.3
	6	1.67	0	32.8
	7	3.33	0	29.4
	8	5.00	0	29.4
150 °C 6 h.	9	0	0	21.6
	10	1.67	0	27.8
	11	3.33	0	25.0
	12	5.00	0	29.6
150 °C 8 h.	13	0	0.9	26.0
	14	1.67	0.9	27.8
	15	3.33	0.9	48.1
	16	5.00	1.2	30.3
200 °C 2 h.	17	0	7.2	26.1
	18	1.67	14.4	28.5
	19	3.33	3.0	29.3
	20	5.00	11.5	27.9

Table B-1 (continued)

Temperature and heating time	Sample No.	Concentration of sodium perborate, phr	% Volatile matter	% Extract
200 °C 4 h.	21	0	13.7	27.5
	22	1.67	21.9	17.1
	23	3.33	14.3	13.6
	24	5.00	11.0	16.2
200 °C 6 h.	25	0	10.4	29.9
	26	1.67	9.9	18.0
	27	3.33	16.1	28.2
	28	5.00	21.3	29.2
200 °C 8 h.	29	0	28.5	28.2
	30	1.67	8.9	31.6
	31	3.33	24.3	33.2
	32	5.00	14.8	27.7
250 °C 2 h.	33	0	24.5	26.1
	34	1.67	24.6	20.3
	35	3.33	24.8	14.1
	36	5.00	21.9	12.4
250 °C 4 h.	37	0	35.4	27.8
	38	1.67	40.0	19.8
	39	3.33	40.3	15.6
	40	5.00	30.8	18.9
250 °C 6 h.	41	0	41.0	18.9
	42	1.67	33.9	19.0
	43	3.33	23.8	25.9
	44	5.00	40.8	24.1

Table B-1 (continued)

Temperature and heating time	Sample No.	Concentration of sodium perborate, phr	% Volatile matter	% Extract
250 °C 8 h.	45	0	42.4	17.2
	46	1.67	48.6	20.5
	47	3.33	55.6	23.5
	48	5.00	29.0	18.8

APPENDIX C

DETERMINATION OF VISCOSITY OF DEGRADED RUBBER

Viscosity of degraded rubber is shown in Table C-1.

Table C-1 Viscosity of degraded rubber

Temperature and heating time	Sample No.	Concentration of sodium perborate, phr	Viscosity of degraded rubber at various shear rates (s^{-1})					
			26.4	66	132	238	290	330
150 °C 2 h.	1	0	0.75	0.66	0.60	0.57	0.55	0.52
	2	1.67	0.75	0.66	0.63	0.62	0.61	0.61
	3	3.33	0.60	0.48	0.46	0.45	0.44	0.42
	4	5.00	0.45	0.42	0.37	0.37	0.37	0.37
150 °C 4 h.	5	0	0.98	0.47	0.31	0.23	0.21	0.21
	6	1.67	0.00	0.00	0.06	0.30	0.60	0.95
	7	3.33	0.00	0.00	0.30	0.67	1.20	1.36
	8	5.00	0.00	0.94	1.46	2.00	2.25	2.73
150 °C 6 h.	9	0	0.55	0.60	0.68	0.83	1.39	1.64
	10	1.67	0.00	0.46	0.86	1.33	1.65	2.05
	11	3.33	0.00	0.42	0.97	1.43	2.22	2.83
	12	5.00	10.8	4.09	2.52	2.15	2.05	1.97
150 °C 8 h.	13	0	0.62	0.75	1.01	1.83	2.25	2.73
	14	1.67	1.50	1.75	2.40	3.21	3.90	4.21
	15	3.33	3.80	3.60	3.37	3.00	2.40	2.32
	16	5.00	2.21	1.98	1.84	1.72	1.69	1.64

Table C-1 (continued)

Temperature and heating time	Sample No.	Concentration of sodium perborate, phr	Viscosity of degraded rubber at various shear rates (s^{-1})					
			26.4	66	132	238	290	330
200 °C 2 h.	17	1	2.40	1.36	1.04	0.21	0.21	0.21
	18	1.67	10.8	6.70	2.04	1.45	1.34	1.27
	19	3.34	11.4	4.90	2.28	1.70	1.60	1.52
	20	5.00	1.20	1.14	0.99	0.95	0.94	0.92
200 °C 4 h.	21	0	2.55	1.65	0.86	0.29	0.23	0.22
	22	1.67	5.42	3.65	0.85	0.79	0.58	0.03
	23	3.33	8.70	4.74	3.27	1.75	1.60	1.56
	24	5.00	10.5	5.30	1.95	1.33	1.31	1.22
200 °C 6 h.	25	0	5.40	3.20	1.02	0.80	0.71	0.50
	26	1.67	3.85	2.55	0.78	0.70	0.68	0.47
	27	3.33	7.50	4.00	0.46	0.44	0.35	0.12
	28	5.00	6.30	3.45	0.42	0.41	0.33	0.08
200 °C 8 h.	29	0	7.50	4.28	1.56	1.07	1.04	1.00
	30	1.67	3.25	2.20	1.43	0.22	0.20	0.11
	31	3.33	1.20	0.60	0.30	0.18	0.14	0.13
	32	5.00	4.20	3.45	2.40	0.25	0.14	0.12
250 °C 2 h.	33	0	10.20	5.70	2.02	1.48	1.36	1.32
	34	1.67	10.30	5.70	1.95	1.37	1.32	1.21
	35	3.33	10.20	4.06	1.98	1.52	1.36	1.28
	36	5.00	10.40	3.60	1.80	1.34	1.20	1.08

Table C-1 (continued)

Temperature and heating time	Sample No.	Concentration of sodium perborate, phr	Viscosity of degraded rubber at various shear rates **(s^{-1})**					
			26.4	66	132	238	290	330
250 °C 4 h.	37	0	10.20	6.32	1.86	1.22	1.15	1.12
	38	1.67	11.80	5.56	1.80	1.22	1.17	1.10
	39	3.33	10.52	4.24	1.82	1.16	1.01	0.96
	40	5.00	10.35	3.50	1.96	0.93	0.90	0.89
250 °C 6 h.	41	0	8.55	5.46	1.92	1.30	1.27	1.25
	42	1.67	9.57	4.90	1.92	1.38	1.02	0.98
	43	3.33	8.86	3.45	1.63	1.33	0.94	0.81
	44	5.00	10.60	4.60	1.83	1.25	1.22	1.18
250 °C 8 h.	45	0	9.60	5.10	1.74	1.08	1.04	0.98
	46	1.67	10.60	4.98	1.82	1.38	1.08	1.01
	47	3.33	11.10	4.98	1.75	1.20	1.16	1.09
	48	5.00	12.50	4.80	1.86	1.25	1.24	1.19

APPENDIX D

DETERMINATION OF BOILING RANGE OF PARAFFIN OIL AND DEGRADED RUBBER

Boiling range of paraffin oil and degraded rubber are shown in Table D-1.

Table D-1 Boiling range of paraffin oil and degraded rubber

% Recovered	Boiling point of degraded rubber °C	Boiling point of paraffin oil °C
0	127.2	294.4
5	174.4	371.1
10	179.4	391.6
15	239.4	403.3
20	274.4	411.6
25	318.3	418.3
30	350.5	423.8
35	374.4	428.8
40	391.6	433.5
45	403.8	438.4
50	413.3	442.5
55	421.1	447.2
60	428.3	452.7
65	435.5	457.1
70	442.7	462.4
75	450.5	468.7
80	458.8	474.3
85	468.3	481.6
90	480.0	490.0
95	498.3	503.3
100	541.6	533.3

APPENDIX E

DETERMINATION OF INITIAL RATE OF RUBBER DEGRADATION

The initial rate of degradation is the molecular weight reduction at initial heating time of 2 h.

Initial rate is calculatedas follows :

Initial rate = (Mo – Mi)/Initial heating time
= (Mo – Mi)/2
where : Mo = Initial molecular weight of NR
Mi = Molecular weight at 2 h of heating time

VITA

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