

Chemical Degradation of Epoxidized Natural Rubber Using Periodic Acid: Preparation of Epoxidized Liquid Natural Rubber

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ABSTRACT: Oxidative degradation of epoxidized natural rubber (ENR) was effectively performed in latex phase by using periodic acid at 30°C. The ENR was prepared from the epoxidation of natural rubber in latex phase using performic acid generated *in situ* by the reaction of hydrogen peroxide and formic acid. The prepared ENR latex was subsequently treated with periodic acid. It was found that the higher the amount of the periodic acid employed the faster the molecular weight of the ENR decreased. Different epoxidation levels of the ENR had no significant effect on the degrada-

tion reaction. Based on ¹H NMR analysis, the epoxide content in the epoxidized liquid natural rubber (ELNR) obtained was about the same as that observed in the ENR before degradation. FT-IR analysis showed an increase in carbonyl signal after prolonged reaction time or when higher amounts of periodic acid were employed. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 6–15, 2005

Key words: degradation; epoxidation; modification; rubber; telechelics

INTRODUCTION

Chemical modifications or functionalizations of polymeric materials are of wide interest to research scientists as they often produce new materials that cannot be prepared or are costly to prepare by means of conventional polymerization reactions. These methods are also used to improve the properties of some commercial polymers or to introduce specific reactive intermediates on the polymer chains for further modification. Epoxide function is considered to be one of the most important intermediate in organic synthesis. The introduction of epoxides on the backbone of natural rubber (NR) will render NR essentially resistant to oil.¹ The epoxide function is also susceptible to various chemical reactions involving hydrogen-donor molecules, such as amines, alcohols, and carboxylic acids. The NR is a high-molecular-weight natural polymer. Therefore, degradation of NR into low-molecular-weight rubber and functionalization with specific functional groups, such as epoxide, would widen the applications of NR. It is possible to lower the molecular weight of the NR before the process of

introducing functional groups to NR is conducted. Oxidative degradation of NR promoted by phenylhydrazine/oxygen system has been reported.² The method was employed by Phinyocheep and Duangthong³ to prepare liquid natural rubber (LNR) before conducting an epoxidation reaction by using performic acid generated *in situ* from the reaction of formic acid and hydrogen peroxide. However, the obtained LNR has a brown color, which may be due to the contamination of the reagents used or to the nonrubber constituents in the NR. Oxidative degradation of deproteinized NR by using potassium persulfate provided the LNR with a light color.^{4,5} However, the epoxidation of deproteinized LNR in latex phase using *in situ* performic acid carried in our laboratory was accompanied by side reactions, such as epoxide ring opening reaction, leading to 1,2-diol unit and formyl addition adducts.

Lead tetraacetate, Pb(OAc)₄ and periodic acid (H₅IO₆) are chemicals of interest used for degradation of the polyisoprenic chain. Typically, both reagents cause cleavage of *vic*-glycols to yield carbonyl compounds. Studied by Burfield and Gan,⁶ Pb(OAc)₄ was found to cause degradation of hydrolyzed epoxidized synthetic rubber (EIR) faster than that of EIR. Synthetic polyisoprene sample (IR), which presumably contains no 1,2-diols, was also slowly degraded by

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Pb(OAc)₄. The authors also found that H₅IO₆ could be employed to degrade NR and acid hydrolyzed NR. In the case of NR, it is believed that the chain degradation arose from the presence of a few 1,2-diol units in the molecular chain. Mauler et al.⁷ investigated chain cleavage of styrene-butadiene rubber (SBR) by using H₅IO₆ and/or ultrasonic radiation. It was found that H₅IO₆ degraded the SBR chain far better than the use of only 40 kHz ultrasonic radiation and it induced degradation of SBR with \bar{M}_w of 325,000 to 80,000. By the use of H₅IO₆ in conjunction with 40 kHz ultrasonic radiation, the \bar{M}_w of SBR was reduced to 40,000. The study of chain cleavage of *cis*-1,4-polyisoprene (*Hevea brasiliensis*) by using H₅IO₆ (2/10 v/v) was carried out by Mauler and coworkers.⁸ They found that the \bar{M}_w of natural rubber was reduced from 800,000 to 5,000 after 60 min when the reaction was performed in chloroform solution at 50°C. H₅IO₆ was also used by Reyx and Campistron⁹ for the preparation of telechelic liquid natural rubber. They found that epoxide content of the starting rubber decreased from 25 to 8% after degradation reaction. The ¹H NMR spectrum revealed the presence of aldehyde and ketone moieties, residual oxiranes, and secondary furanic and cyclic structures. Gillier-Ritoit *et al.*¹⁰ investigated chain degradation of polyisoprene (PI) and epoxidized polyisoprene (EPI) using H₅IO₆ in organic solvent (THF). The degraded PI gave ¹H NMR characteristics similar to those of degraded EPI. It should be noted that the method produced degraded rubber containing aldehyde and ketone terminal ends.

In view of the potential benefit that periodic acid is soluble in water, the purpose of the work described below is to determine whether the reagent would allow chain scission of epoxidized natural rubber (ENR) in latex phase for the preparation of epoxidized liquid natural rubber (ELNR). To minimize the unwanted reactions or contamination from nonrubber constituents in the NR, purification of NR latex by treatment with proteinase enzyme followed by double centrifugation was carried out prior to the degradation process. The purified natural rubber (PNR) was epoxidized by performic acid in latex phase to give epoxidized purified natural rubber (ENR) in latex phase, which was subsequently treated with periodic acid. The effects of the amounts of periodic acid employed and the types of ENR on the degradation reaction were also investigated.

EXPERIMENTAL

Materials

High ammonia natural rubber (HANR) latex [dry rubber content (DRC) = 60%] was purchased from Bangkok Rubber Company, Thailand. Proteinase enzyme B KP 3939 was supplied by Kao Co. Ltd. Non-

ylphenoxy poly(ethylene oxide) (Sinnopal NP 307) was supplied by Cognis Company. Formic acid and hydrogen peroxide were purchased from Merck and Ajax Chemicals, respectively. Periodic acid was purchased from Acros Organics.

Preparation of purified natural rubber

PNR was prepared by stirring the HANR latex diluted to 30% DRC, with 0.04% (w/v) proteinase enzyme B KP 3939 and 1% (w/v) Sinnopal NP 307 surfactant at 37°C for 24 h. The NR latex was then centrifuged by an ultracentrifuge machine (13,000 rpm). The cream fraction was isolated and redispersed in 0.5% (w/v) surfactant. The redispersed latex was recentrifuged and the PNR in the form of the cream fraction was redispersed in 0.5% (w/v) surfactant and was kept in latex form for further reaction.

Preparation of epoxidized natural rubber

PNR latex (20% DRC) was stabilized by 3.5 phr of Sinnopal NP 307 as a nonionic surfactant at room temperature for 15 h before epoxidation. The epoxidation was carried out in a 250-ml glass reactor equipped with a controlled speed stirrer of 300 rpm. The latex was heated to 60°C before adding the desired amount of formic acid ([HCOOH]/[polyisoprene unit] = 0.1 or 0.3 mol.mol⁻¹). The latex was stirred for 15 min, before hydrogen peroxide ([H₂O₂]/[polyisoprene unit] = 0.1 or 0.3 mol.mol⁻¹) was slowly added. The reaction was allowed to proceed for 24 h.

Oxidative degradation by periodic acid

The ENR in latex phase (20% DRC) from the previous step was treated with a specific amount of periodic acid (H₅IO₆) at 30°C. At varying reaction times, the degraded rubber was sampled and precipitated in methanol. The rubber was reprecipitated from a couple of dichloromethane and methanol. The liquid rubber obtained after drying in a vacuum at room temperature was a light yellow color.

Characterization

Intrinsic viscosity [η] of natural rubber and its modified forms was evaluated by using an Ubbelohde viscometer (capillary diameter 0.53 mm). The conditions of measurement were 0.1–0.2 g/dl of the rubber in toluene solution at 30°C.

Gel permeation chromatography (GPC) (Waters) was used to measure the weight average molecular weight (\bar{M}_w) and number average molecular weight (\bar{M}_n) of the degraded rubbers. The system was operated at 30°C using THF as an eluent and polystyrenes as standard calibrators. The machine is equipped with

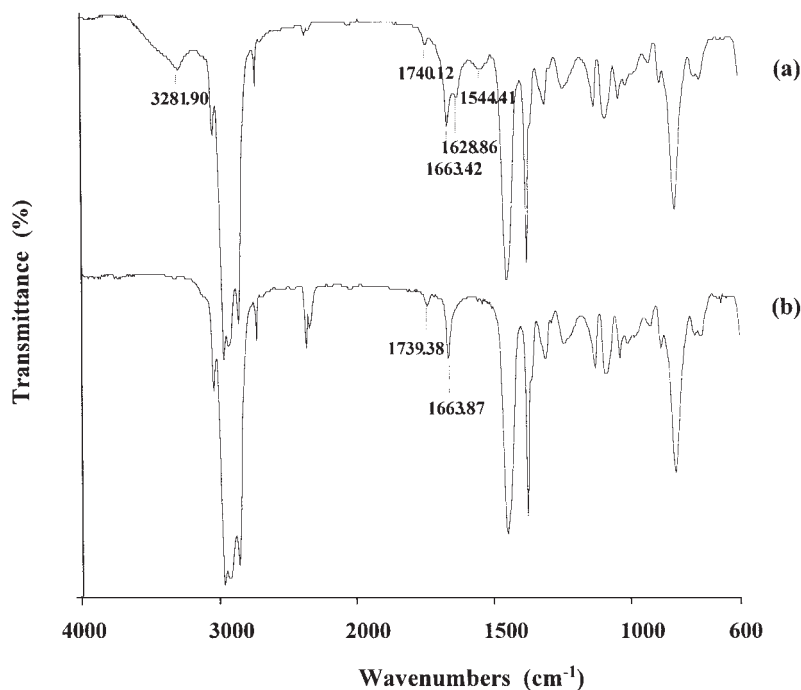


Figure 1 Infrared spectra of (a) natural rubber (NR) and (b) purified liquid natural rubber (PNR).

a differential refractometer detector (RD) and an ultraviolet detector (UV 1000).

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrophotometer using direct film casting on a NaCl cell. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300 (300 MHz).

RESULTS AND DISCUSSION

Epoxidation reaction

Generally, dried rubber obtained from evaporation or coagulation of HANR latex has a pale brown color. Purification of NR by enzymatic treatment, surfactant washing, and double ultracentrifugation resulted in rubber with a light yellow color. The process might eliminate some nonrubber components such as β -carotenoid pigment. The infrared spectrum of the PNR in Figure 1(b) indicates the disappearance of characteristic amide bands at $3,282\text{ cm}^{-1}$ (N-H stretching), $1,629\text{ cm}^{-1}$ (amide I vibration), and $1,544\text{ cm}^{-1}$ (amide II vibration) compared to the infrared spectrum of NR in Figure 1(a). This could be attributed to the decrease of some proteins in NR.^{5,11} This result is in accordance with the decrease of nitrogen content (%) measured by micro-Kjeldahl technique from 0.4% of NR to 0.03% for PNR. Therefore, partial elimination of proteins in NR latex was accomplished. As a result, the intrinsic viscosity $[\eta]$ of NR was 5.88 and it was reduced to 4.31 for PNR.

Epoxidation of PNR was carried out in latex phase using performic acid formed *in-situ* by the reaction of hydrogen peroxide and formic acid.³ The chemical structure of ENR was analyzed by infrared spectroscopy and ^1H NMR. The infrared spectrum of ENR in Figure 2(a) indicates the appearance of characteristic signals of epoxide ring at $1,249\text{ cm}^{-1}$ (symmetric stretching of epoxide ring) and 870 cm^{-1} (asymmetric stretching of epoxide ring). The ^1H NMR spectrum of ENR in Figure 3 shows the presence of signals at 5.1 and 2.7 ppm, assigned to the olefinic proton of *cis*-1,4-polyisoprenic structure and the methine proton adjacent to the epoxide ring, respectively. The signals of methyl and methylene groups adjacent to the epoxide unit were observed at 1.26 and 2.16 ppm, respectively. The residual unreacted unsaturation exhibited the signals of methyl and methylene protons next to the carbon-carbon double bond at 1.67 and 2.09 ppm, respectively. The degree of epoxidation was determined by comparing the integration area of the methine proton adjacent to the oxirane ring at 2.7 ppm and that of the proton adjacent to the carbon-carbon double bond of polyisoprenic structure at 5.1 ppm.^{3,12-14} By varying the amounts of formic acid and hydrogen peroxide at a particular reaction temperature and time, the degree of epoxidation in the ENR was affected. Several types of ENR latex, i.e., 5 and 18–20% ENR were prepared for further investigation of the reaction with periodic acid. In all ENR samples obtained, no observation of signals corresponding to side reactions such as formation of diol and furan, as

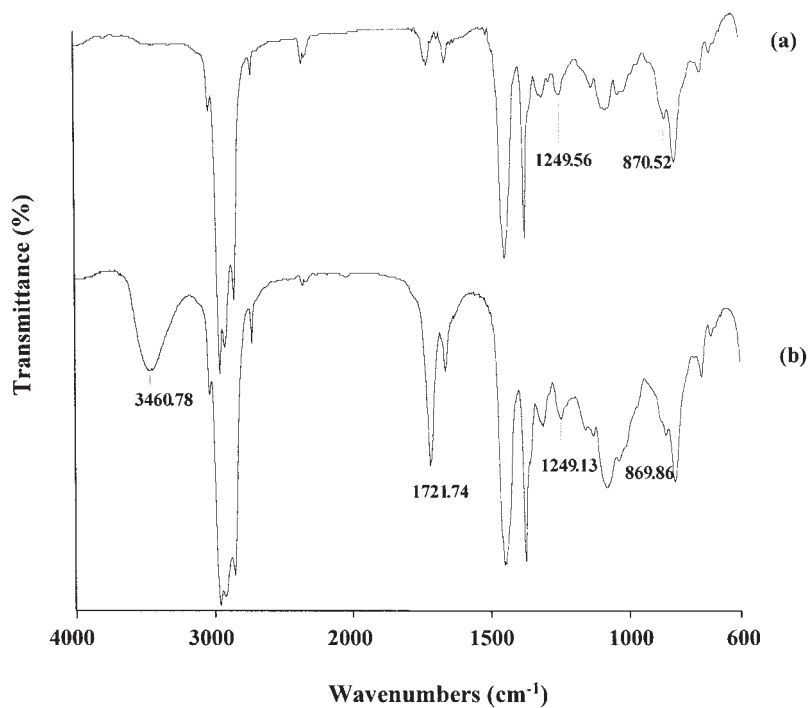


Figure 2 Infrared spectra of (a) epoxidized natural rubber (ENR) and (b) epoxidized liquid natural rubber (ELNR).

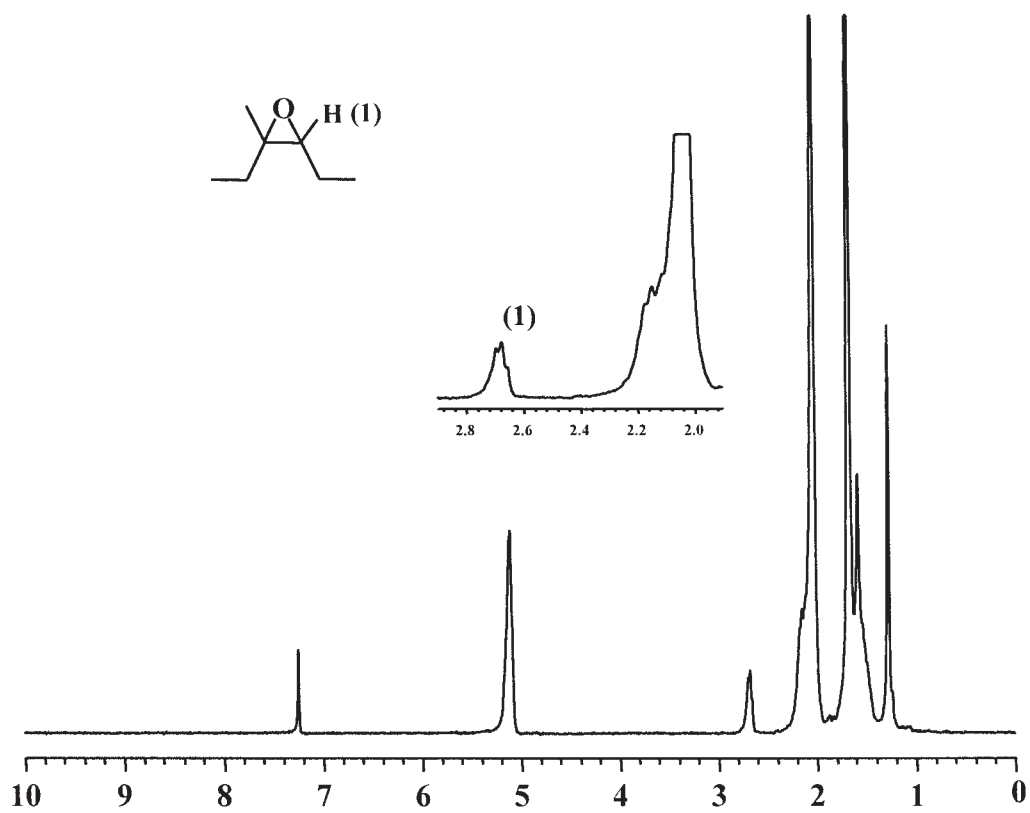


Figure 3 ¹H NMR spectrum of epoxidized natural rubber (ENR).

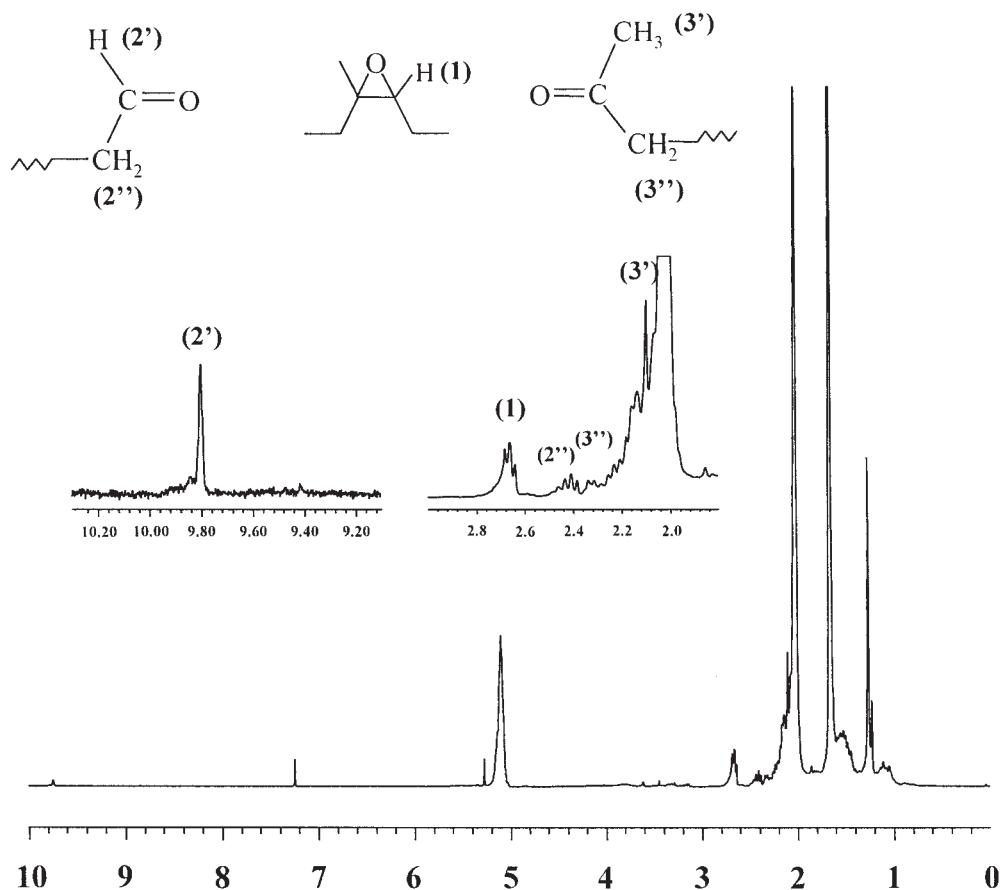


Figure 4 ^1H NMR spectrum of epoxidized liquid natural rubber (ELNR).

previously mentioned in the literature was detected in ^1H NMR.^{15–17}

Oxidative degradation reaction

To promote chain degradation, the ENR latex prepared as discussed in the previous section was subsequently treated with periodic acid (H_5IO_6) at 30°C . Infrared spectra of ENR starting material and the degraded ENR (ELNR) were compared as shown in Figure 2. The obtained ELNR exhibited the characteristic signals of the presence of epoxide unit at 870 and $1,249\text{ cm}^{-1}$ similar to those observed in the ENR. This implied that epoxide moieties still remained after degradation process. The strong signal at $1,721$ and $3,460\text{ cm}^{-1}$ indicated the presence of carbonyl group ($\text{C}=\text{O}$) and hydroxyl function ($\text{O}-\text{H}$).

The microstructure of the ELNR was further analyzed based on ^1H and ^{13}C NMR data as shown in Figures 4 and 5, respectively. The characteristics of olefinic and oxirane methine protons in ^1H NMR spectrum gave rise to signals at 5.14 and 2.7 ppm, respectively. The signals of methyl and methylene protons of the epoxidized and polyisoprenic units were detected at the chemical shifts discussed in the previous sec-

tion. The appearance of new signals was observed at 2.1, 2.2–2.5, and 9.8 ppm. They were assigned to the signals of the three types of protons adjacent to carbonyl functions: $\text{CH}_3-\text{C}=\text{O}$, $-\text{CH}_2-\text{C}=\text{O}$, and $\text{H}-\text{C}=\text{O}$, respectively, as presented in Figure 4. These signals are in agreement with the strong absorption peak of carbonyl function observed in the IR spectrum of the ELNR. This observation is in accordance with work reported in the literature.¹⁰ At this point, it is believed that the chemical structure of the ELNR is composed of $\text{C}=\text{C}$ of the isoprene unit, epoxidized structure, ketone, and aldehyde end. According to ^{13}C NMR analysis, the presence of the epoxidized structure on the liquid rubber was evidenced by the signals at 64.8 ppm (oxirane tertiary carbon) and 60.5 ppm (oxirane secondary carbon) (Fig. 5). Signals at 202.1 and 208.7 ppm confirmed the existence of aldehyde and ketone function, respectively. Therefore, telechelic rubber could be obtained.

The molecular weight of the rubber after the reaction with periodic acid was reduced depending on the reaction time. The molecular weight and the amount of epoxide content observed after degradation of ENR latex performed with $[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}]$ equal to $0.51\text{ mol}\cdot\text{mol}^{-1}$ are presented in Table I. Significant

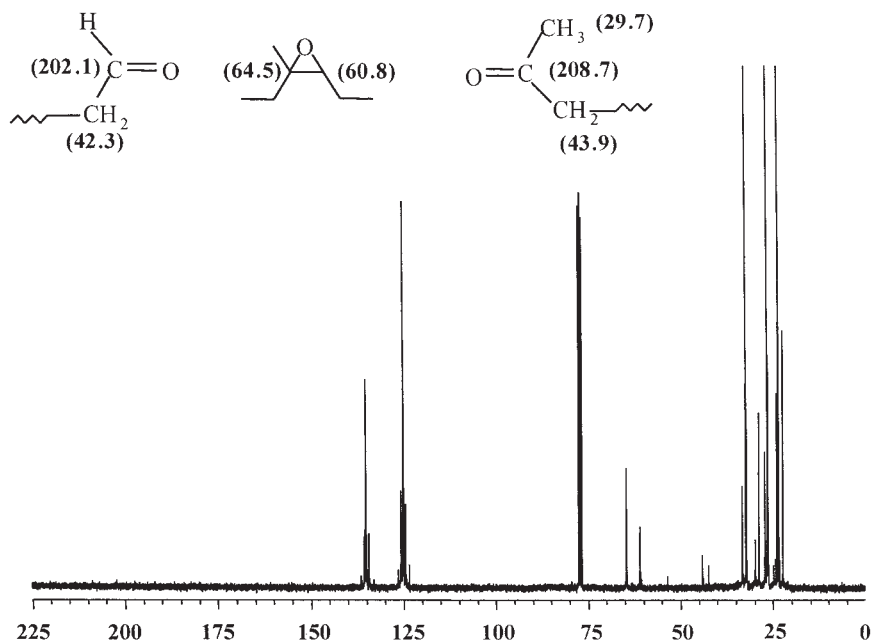


Figure 5 ^{13}C NMR spectrum of epoxidized liquid natural rubber (ELNR).

reduction of both \bar{M}_w and \bar{M}_n of ENR after a few hours of reaction was observed. However, the rate of the reduction slowed down at extended reaction times (after 12 h). This degradation process proceeded at a considerably lower temperature (30°C) than the degradation promoted by phenylhydrazine (60°C) and potassium persulfate (60°C).^{3,5} These results are in accordance with the results reported previously in the literature that the periodic acid causes hydrocarbon chain degradation.^{7,8,10} It was also found that the ELNR obtained at various reaction times possesses approximately the same degree of epoxide unit as found in the starting material. This implied that the degradation reaction of the ENR by periodic acid did not take place at the epoxide function as previously

discussed. Therefore, the degradation reaction seemingly occurred at other parts of the molecular chain. The obtained liquid rubber contained ketone and aldehyde functional ends, suggesting that telechelic epoxidized liquid rubber was formed.

Parameters affecting the degradation reaction

Amount of periodic acid

The degradation of ENR latex using various amounts of periodic acid ($[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}] = 0.24, 0.51$ and $1.13 \text{ mol}\cdot\text{mol}^{-1}$) at 30°C was studied and the FT-IR spectra of the resulting products after 21 h of degradation reaction are shown in Figure 6. In all cases degraded rubber exhibited the absorption peaks of oxirane and carbonyl functions at 870 and 1,718 cm^{-1} , respectively. It should be emphasized that, at higher amounts of H_5IO_6 employed, the absorption intensity of the carbonyl function at 1,718 cm^{-1} is increased compared to the absorption band of $\text{C}=\text{C}$ unit of isoprene at 1,668 cm^{-1} . In addition, the increase in the absorption signal at 3,460 cm^{-1} assigned to the O-H moiety was also detected. It was postulated that, upon treatment of ENR with periodic acid, the oxidation of the rubber chain took place prior to the periodic acid further oxidizing the *vic*-diols into degraded rubber containing aldehyde and ketone functions at chain ends.^{18,19}

The use of a small amount of the periodic acid ($[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}] = 0.24 \text{ mol}\cdot\text{mol}^{-1}$) gave no significant effect on the ENR degradation. A very weak signal of carbonyl function was observed by IR

TABLE I
Results of Epoxide Content, Average Molecular Weight, and Polydispersity Index of Degradation of ENR (20.4% Epoxide Content) at Various Reaction Times

Reaction time (h)	$[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}] = 0.51 \text{ mol}\cdot\text{mol}^{-1}$			
	Epoxide content (%)	\bar{M}_w ($\times 10^4$)	\bar{M}_n ($\times 10^4$)	I^a
0	20.4	91.41 ^b	14.58 ^b	6.27
2	20.4	26.36	1.11	23.79
4	22.2	12.41	0.68	18.17
8	21.8	9.89	0.74	13.28
12	21.4	4.98	0.52	9.67
21	21.6	4.45	0.45	9.86
30	19.8	4.16	0.46	9

^a Polydispersity index.

^b Calculated relative to $[\eta]$ using the method reported in the literature.⁵

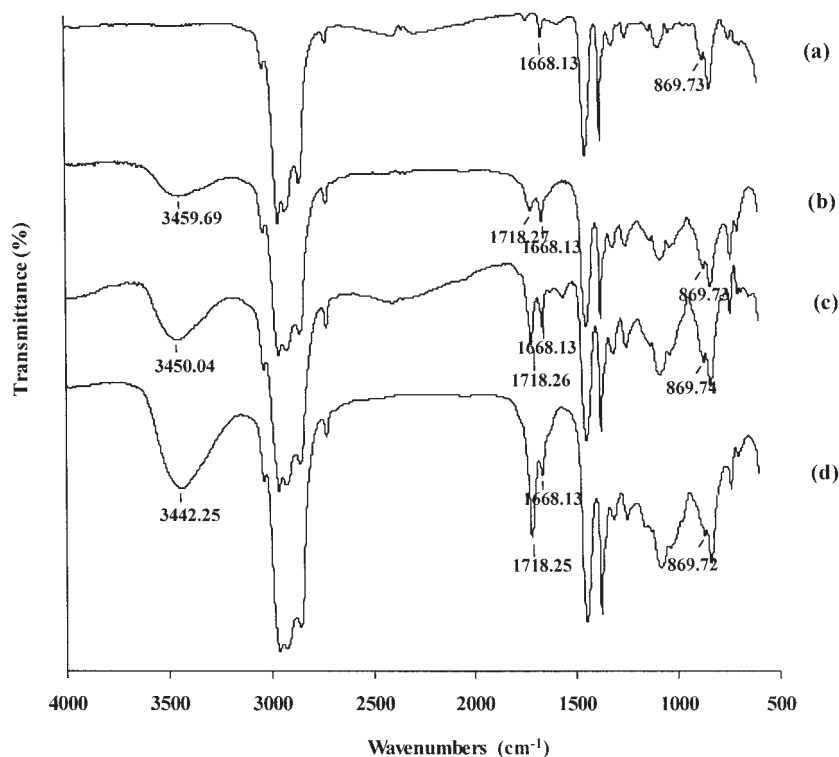


Figure 6 Infrared spectra of (a) epoxidized natural rubber (ENR), (b) degraded ENR using $[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}] = 0.24 \text{ mol.mol}^{-1}$, (c) degraded ENR using $[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}] = 0.51 \text{ mol.mol}^{-1}$, and (d) degraded ENR using $[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}] = 1.13 \text{ mol.mol}^{-1}$.

analysis after 21 h. Tables I and II show the obtained molecular weight (\bar{M}_w and \bar{M}_n) and the epoxide content of the degraded rubbers by using $[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}]$ equal to 0.51 and 1.13 mol.mol^{-1} , respectively. It can be seen that, by using $[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}]$ equal to 1.13 mol.mol^{-1} , the \bar{M}_w of ENR was significantly decreased from 91.41 to 28.54 and 14.03×10^4 after 10 min (0.167 h) and 2 h of the reaction time, respectively (Table II). While using

$[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}]$ equal to 0.51 mol.mol^{-1} , the \bar{M}_w of ENR was found to be 26.36×10^4 after 2 h of the reaction time (Table I). It can be postulated that the degradation of the ENR by using $[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}]$ of 1.13 mol.mol^{-1} was faster than the use of $[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}]$ equal to 0.51 mol.mol^{-1} . The degradation reaction was allowed to proceed until it reached the maximum degree of degradation (12 h). The liquid rubber obtained was colorless and transparent. There was no significant further reduction in the molecular weight when the reaction time was extended to 21 and 30 h. The degraded rubber had an \bar{M}_n of about 5,000 in both cases. However, it was noticed in both cases that the absorption intensity of the signal for the carbonyl group increased upon a prolonged reaction time. In addition, as the amounts of periodic acid increased, the intensity of carbonyl signal also increased. It was proposed that the periodic acid might act as a reagent for chain scission and as an oxidizing agent as well.

Epoxide content

The effect of the amount of epoxide group in the rubber chain on the degradation was investigated by using ENR(5) containing a small amount of epoxide groups (5.0%) compared with ENR(18) containing

TABLE II
Results of Epoxide Content, Average Molecular Weight, and Polydispersity Index of Degradation of ENR (18.6% Epoxide Content) at Various Reaction Times

Reaction time (h)	$[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}] = 1.13 \text{ mol.mol}^{-1}$			
	Epoxide content (%)	\bar{M}_w ($\times 10^4$)	\bar{M}_n ($\times 10^4$)	I^a
0	18.6	91.41 ^b	14.58 ^b	6.27
0.167	18.6	28.54	3.74	7.64
2	18.2	14.03	1.76	7.97
4	17.6	9.97	1.48	6.74
8	17.7	8.44	0.39	21.62
12	17.1	4.16	0.50	8.39
21	17.7	3.64	0.51	7.08

^a Polydispersity index.

^b Calculated relative to $[\eta]$ using the method reported in the literature.⁵

TABLE III
Results of Epoxide Content, Average Molecular Weight, and Polydispersity Index of Degradation of ENR(18)
(18.6% Epoxide Content) and ENR(5) (5% Epoxide Content)

Reaction time (h)	ENR(5) $[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}] = 4.06$ mol.mol ⁻¹				ENR(18) $[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}] = 1.13$ mol.mol ⁻¹			
	Epoxide content (%)	\bar{M}_w ($\times 10^4$)	\bar{M}_n ($\times 10^4$)	I ^a	Epoxide content (%)	\bar{M}_w ($\times 10^4$)	\bar{M}_n ($\times 10^4$)	I ^a
0	5.0	93.16 ^b	14.85 ^b	6.27	18.6	91.41 ^b	14.58 ^b	6.27
21	6.0	3.76	0.55	6.89	17.7	3.64	0.51	7.08

^a Polydispersity index.

^b Calculated relative to $[\eta]$ using the method reported in the literature.⁵

18.6% epoxide content. An excess amount of periodic acid compared to the epoxide content was employed. The ratios of $[\text{H}_5\text{IO}_6]/[\text{epoxidized unit}]$ equal to 4.06 and 1.13 mol.mol⁻¹ were treated with ENR(5) and ENR(18), respectively. After 21 h of reaction, the \bar{M}_n of the degraded ENR(5) obtained was about 5,000, which was similar to the molecular weight of the degraded ENR(18) obtained as shown in Table III. The resulting rubbers of ENR5 and ENR18 did not show a significant change in the amounts of the epoxide content at various reaction times compared to the starting materials. These results may support that the degradation by periodic acid did not take place at the epoxide function but that it seems likely to have occurred via the C=C of the isoprene unit with an appropriate intermediate such as *vic*-diols, as reported in the degradation of small *vic*-diol molecules.^{18,19}

Types of rubber

The treatment of periodic acid with NR and PNR was also investigated compared to the reaction with ENR. $[\text{H}_5\text{IO}_6]/[\text{polyisoprene unit}]$ equal to 0.2 mol.mol⁻¹ was applied to NR and PNR and the results of degradation are shown in Tables IV and V. The results show that periodic acid caused the breakage of NR and PNR

rubber chains but not with as high efficiency as in the case of the epoxidized rubber, as after 8 h of reaction time the \bar{M}_w of degraded NR and PNR were only 15.87 and 13.85×10^4 , respectively, while the degraded ENR was found to be 9.89×10^4 (Table II). The ¹H NMR analysis of the degraded rubbers (NR and PNR) showed the presence of approximately 3% of epoxide content in both cases. The periodic acid might be able to introduce an epoxide functional group onto the rubber molecule but at a very small quantity. It can be postulated that the degradation rate of NR and PNR by periodic acid is far lower than that of the ENR. As the periodic degradation reaction was carried out in latex phase, it might be proposed that the ENR has higher polarity than the NR and PNR, therefore the polar molecule like periodic acid is more compatible with ENR than NR and PNR, hence the degradation process of ENR is faster than in the case of NR and PNR.

The degradation of PNR by periodic acid in the presence of H₂O₂ was also carried out. Table VI shows that degradation of the PNR in the presence of H₂O₂ was faster than the reaction without H₂O₂ (Table V), i.e., lower molecular weight of the rubber was obtained at the same reaction time of 8 h. It should be noted that the obtained liquid rubbers in the former

TABLE IV
Results of Epoxide Content and Average Molecular Weight of Degradation of NR Using
 $[\text{H}_5\text{IO}_6]/[\text{Polyisoprene Unit}] = 0.2$ mol.mol⁻¹
at Various Reaction Times

Reaction time (h)	$[\text{H}_5\text{IO}_6]/[\text{polyisoprene unit}] = 0.2$ mol.mol ⁻¹			
	Epoxide content (%)	$[\eta]$	\bar{M}_w ($\times 10^4$) ^a	\bar{M}_n ($\times 10^4$) ^a
0	0	5.88	129.49	20.62
8	0	0.59	15.87	2.53
12	0	0.43	11.75	1.90
21	2.6	0.33	9.16	1.46
30	2.6	0.22	6.38	1.02

^a Calculated relative to $[\eta]$ using the method reported in the literature.⁵

TABLE V
Results of Epoxide Content and Average Molecular Weight of Degradation of PNR Using
 $[\text{H}_5\text{IO}_6]/[\text{Polyisoprene Unit}] = 0.2$ mol.mol⁻¹
at Various Reaction Times

Reaction time (h)	$[\text{H}_5\text{IO}_6]/[\text{polyisoprene unit}] = 0.2$ mol.mol ⁻¹			
	Epoxide content (%)	$[\eta]$	\bar{M}_w ($\times 10^4$) ^a	\bar{M}_n ($\times 10^4$) ^a
0	0	4.31	97.43	15.51
8	3.5	0.51	13.85	2.21
12	3.2	0.33	9.28	1.48
21	2.6	0.24	6.92	1.10
30	2.7	0.22	6.32	1.01

^a Calculated relative to $[\eta]$ using the method reported in the literature.⁵

TABLE VI
Results of Epoxide Content and Average Molecular Weight of Degradation of PNR Using $[H_5IO_6]/[Polyisoprene\ Unit] = 0.2\ mol.mol^{-1}$ and $[H_2O_2]/[Polyisoprene\ Unit] = 0.3\ mol.mol^{-1}$ at Various Reaction Times

Reaction time (h)	$[H_5IO_6]/[polyisoprene\ unit] = 0.2\ mol.mol^{-1}$			
	Epoxide content (%)	$[\eta]$	\bar{M}_w ($\times 10^4$)*	\bar{M}_n ($\times 10^4$)*
0	0	4.31	97.43	15.51
2	0	0.45	12.21	1.94
4	5.9	0.37	10.31	1.64
8	5.5	0.27	7.62	1.21
12	7.1	0.19	5.69	0.91
21	6.7	0.15	4.45	0.71
30	5.8	0.13	3.89	0.62

* Calculated relative to $[\eta]$ using the method reported in the literature.⁵

case are composed of higher epoxide content (about 6%) than those obtained without the addition of H_2O_2 (about 3% epoxide content). It was reported in the literature that H_2O_2 alone could epoxidize low-molecular-weight alkene but it gave no significant epoxida-

tion to high ammonia-concentrated natural latex at room temperature.²⁰ It can be postulated that the rate of rubber degradation by using periodic acid for various types of rubbers was found to be in the order of $ENR + H_5IO_6 > PNR + H_5IO_6 + H_2O_2 > PNR + H_5IO_6 > NR + H_5IO_6$.

Proposed degradation pathway by periodic acid

Generally, periodic acid is effectively employed for carbon-carbon scission of organic compounds containing a *vic*-diol structure.^{18,19,21} However, several reports in the literature have indicated that periodic acid caused chain degradation of dienic homopolymers such as NR and synthetic polyisoprene and copolymers such as SBR. Mauler et al.^{7,8} had explained that the reduction of the molecular weight of SBR and NR by periodic acid took place at the $C=C$ moieties presented in the molecular chains. Nevertheless, the authors did not propose the reaction pathway. Gillier-Ritoit *et al.*¹⁰ found that the chain cleavage of PI with H_5IO_6 was slower than that of EPI. They proposed that the H_5IO_6 cleaved the EPI directly through the transformation of epoxide function into *vic*-diol but, in the

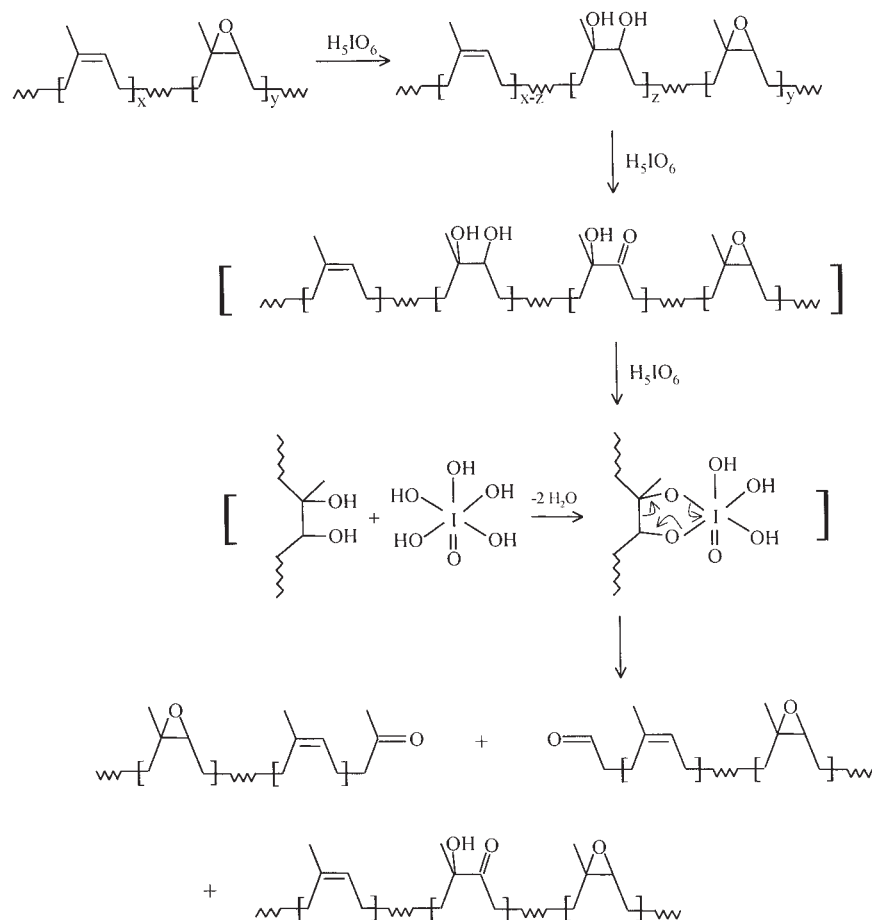


Figure 7 Proposed reaction pathway of oxidative degradation of epoxidized rubber by periodic acid.

case of chain degradation of PI, they proposed a two-step mechanism. In the first step, H_5IO_6 reacted with the double bond, resulting in an epoxide or an α -glycol structure. The epoxide or α -glycol then was cleaved by a second equivalent of H_5IO_6 . In our case, the epoxide contents before and after degradation of the ENR were approximately the same in all of the conditions used. The degradation process might not take place at the epoxide ring. If it did take place, the degree of degradation should have depended on the degree of epoxidation. In addition, the chain degradation also occurred in the cases of NR and PNR, which do not contain the epoxide group on the molecular chain. Depending on the specific conditions selected, treatment of potassium permanganate with olefinic compounds can lead to several types of modified products, such as *vic*-diol, α -hydroxy ketone, and degraded compounds having carbonyl functional ends.²² Similar in structure as the permanganate, the periodate might be able to function in a similar manner. Increasing the amounts of periodic acid and reaction times, the increase of carbonyl and hydroxyl signals was observed. In addition, at prolonged reaction times, the degradation seemed to slow down but the intensity of the carbonyl signal of the degraded rubber increased. Therefore the degradation pathway of oxidative degradation of ENR by periodic acid as shown in Figure 7 could be proposed. The periodic acid might oxidize the double bond of the ENR into *vic*-diols. The carbon-carbon of the *vic*-diols were then partially cleaved by other molecules of periodic acid, resulting in chain degradation forming aldehyde and ketone functional ends. The *vic*-diols could be also oxidized by periodic acid forming α -hydroxyl ketone, which was evidenced by the appearance of hydroxyl and ketone signals in the IR spectrum as discussed in the former section. The presence of the epoxide group in the rubber chain may accelerate the degradation due to the increased polarity of the rubber.

CONCLUSION

Low-molecular-weight rubber containing epoxide functions can be effectively prepared by oxidative degradation of ENR in latex phase using periodic acid (H_5IO_6) at low temperature (30°C). The molecular weight of ENR was significantly decreased after 10 min of reaction time by using $[H_5IO_6]/[\text{epoxidized unit}]$ equal to 1.13 mol.mol⁻¹. The M_n of ENR and

ELNR after 10 min of degradation was 14.58 and 3.74 $\times 10^4$, respectively. The epoxide content of the liquid rubbers was approximately the same as that of the ENR starting materials. The NR and PNR, which did not contain the epoxide group, were also degraded by H_5IO_6 . The degraded rubber obtained from different types of rubbers, i.e., NR, PNR, and ENR latex, are considered to be telechelic liquid rubber containing aldehyde at one end and ketone at the other end of the rubber chain. The evidence obtained from IR and ¹H and ¹³C NMR of the degraded rubbers could be used to propose that the degradation reaction of the unsaturated rubber by periodic acid occurred at the double bond of the rubber molecule.

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