# PREPARATION OF PHOTOSENSITIVE ELASTOMER FROM LIQUID NATURAL RUBBER

# การเตรียมอิลาสโทเมอร์ที่ไวต่อแสงจากยางธรรมชาติเหลว

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## ABSTRACT

*Photo-induced polymerization reaction had been widely interested by macromolecular chemists and technologists because of the rapid chemical reaction and the ability to be carried in solution or solid state at room or high temperature. In this work photocrosslinkable elastomers were prepared by addition reaction of photosensitive acid onto epoxidised liquid natural rubber (ELNR). ELNR was prepared by two step reactions: first natural rubber was depolymerized into liquid natural rubber (LNR) by using* $O_2$*/phenylhydrazine system at 60°C, then hydrogen peroxide and formic acid were added to LNR at 55°C to epoxidise the LNR. The addition reaction of photosensitive acid such as acrylic acid, methacrylic acid and cinnamic acid onto ELNR were carried out in* $CHCl_3$ *at 80°C. The kinetic of addition reaction was followed by titration of residual acid with 0.1M KOH. The acid grafted onto ELNR was obtained by precipitation in methanol. The results showed that addition reaction of cinnamic acid was slower than acrylic acid and methacrylic acid. The increase of temperature led to slight improvement in the grafting efficiency. Furthermore, the molecular weight of ELNR had also influence on the rate of addition reaction of acid. It was found that the reaction times of low molecular weight ELNR were shorter than those of high molecular weight ELNR. Photocrosslinking study of cinnamated ELNR by ultra-violet radiation showed the rate of photocrosslinking, as followed by IR spectroscopy, to be dependent on molecular weight, thickness and percentage of cinnamate grafted to the polymer chain.*

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## บทคัดย่อ

การทำปฏิกิริยาและการเกิดพอลิเมอร์ด้วยแสง เป็นที่สนใจกันอย่างกว้างขวางทั้งในกลุ่มนักเคมี และนักเทคโนโลยี เนื่องจากเป็นปฏิกิริยาที่ทำได้อย่างรวดเร็วและสามารถทำได้ทั้งในรูปของเหลวและของแข็ง ทั้งในสภาวะอุณหภูมิปกติหรืออุณหภูมิสูงกว่าปกติ การวิจัยนี้ เป็นการเตรียมพอลิเมอร์ที่สามารถเกิดโครงสร้างร่างแหด้วยแสง โดยใส่หมู่อนุมูลที่ไวต่อแสงลงบน Epoxidised liquid natural rubber (ELNR) การเตรียม ELNR จะแบ่งออกเป็น 2 ขั้นตอน คือ การเตรียมยางธรรมชาติเหลว (LNR) โดยใช้ phenylhydrazine/$O_2$ ที่อุณหภูมิ 60°ซ. จากนั้นเติมกรดฟอร์มิก และไฮโดรเจนเพอร์ออกไซด์ ลงใน LNR ที่เตรียมได้ที่อุณหภูมิ 55°ซ. เพื่อทำการ epoxidise LNR นำ ELNR ที่เตรียมได้มาทำปฏิกิริยา ด้วยการเติมกรดที่ไวต่อแสง เช่น กรดอะครายลิก กรดเมทาอะครายลิก และกรดซินนามิก การเปิด epoxide ring ของ ELNR จะทำในรูปของสารละลายในคลอโรฟอร์ม ที่อุณหภูมิ 80°ซ. ทำการศึกษาปฏิกิริยาที่ดำเนินไปโดยใช้วิธีการทางโพเทนซิออเมตริกไทเทรชัน (potentiometric titration) ด้วย alcoholic KOH เพื่อหาปริมาณกรดที่ลดลงจนเกิดปฏิกิริยาสมบูรณ์ สาร photocurable elastomer ที่ได้เมื่อสิ้นสุดปฏิกิริยาจะถูกทำให้ตกตะกอนด้วยเมทานอล จากผลการทดลองพบว่าเมื่อเติมกรดซินนามิกปฏิกิริยาเกิดได้ช้ากว่ากรดอะครายลิก และกรดเมทาอะครายลิก โดยที่การเพิ่มของอุณหภูมิไม่ค่อยมีผลต่อปริมาณการเกิดกราฟทิง (grafting) นอกจากนั้นน้ำหนักโมเลกุลของพอลิเมอร์ก็จะมีผลต่ออัตราการเกิดปฏิกิริยา ซึ่งพบว่าพอลิเมอร์ที่น้ำหนักโมเลกุลน้อยกว่าจะเกิดปฏิกิริยาได้เร็วกว่าพอลิเมอร์ที่มีน้ำหนักโมเลกุลมากกว่า และจากการศึกษาการเกิดปฏิกิริยา photocrosslinking ด้วยแสงอุลตราไวโอเลต โดยใช้ยางที่ได้จากการดัดแปรโดยกรดซินนามิก ด้วยเครื่องมือทาง IR spectroscopy พบว่าอัตราการเกิด photocrosslinking จะขึ้นอยู่กับน้ำหนักโมเลกุล ความหนาของพอลิเมอร์ที่นำมาฉายแสง และเปอร์เซ็นต์ของกลุ่มที่ไวต่อแสงบนสายโซ่พอลิเมอร์

## INTRODUCTION

The original of liquid natural rubber dated back tò 1923 by mechano-chemical degradation of solid natural rubber[8,18]. It found application in the field of adhesives[5]. The study of photochemical depolymerization of rubber had been carried out by MRPRA, allowing short polyisoprenic chain with carboxylic ends. Ozonolysis was another reaction that caused degradation of the rubber chain. Institut de la Recherche Applique sur les Polymeres (IRAP) in France developed a method of preparation of LNR based on oxidative degradation reaction of natural rubber in the latex state at a moderate temperature by using phenylhydrazine and oxygen system. Pautrat *et al.* studied influence of different parameters of oxidative degradation of natural rubber. They found that the molecular weight of LNR obtained was effected by the following parameters : amount of phenylhydrazine, rate of air flow, reaction time, and temperature of the reaction.

P. Khunkamchoo[11] repeated the work on preparation of LNR from latex phase and found further that molecular weight of LNR was influenced by another two parameters : nonrubber constituents and metal ions.

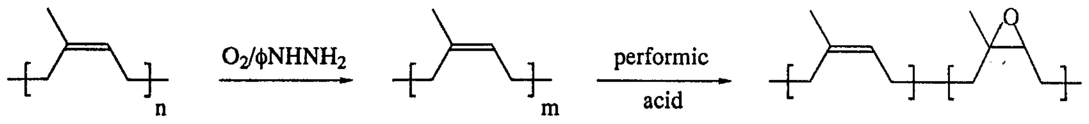
The mechanism of the degradation had been generally proposed by Shelton[19] as the followings : oxidation of phenylhydrazine and the oxidative degradation of polyisoprenic structure.[15,19]

The reactions of natural rubber and other unsaturated polymers with epoxidising reagents had been widely studied.[10] In the field of natural rubber, the epoxidation could be performed by in-situ or preformed peracids and NR could be applied in different physical state such as in solution or in latex state. The chemistry of epoxidation of NR with preformed peracetic acid and in-situ performic acid had been mostly studied.[1] It was found that epoxidation of NR with peroxy acid in homogenous solution such as chloroform and toluene and in latex occurred without mainchain fission or isomerization of the cis configuration of isoprenic structure.[9]

However, it was known that secondary ring opening reaction of the initially formed epoxide group could occur in the epoxidation of unsaturated low molecular weight compound.[21] In the case of epoxidation of natural rubber, it had been revealed that two distinct types of ring opening products were obtained depending on the level of epoxidation.

Different parameters of epoxidation of natural rubber latex had also been studied such as concentration of peroxy acid, latex or solid content, type of surfactant. In the strong in situ epoxidation of natural rubber latex using formic acid-hydrogen peroxide[3] with varying latex concentration from 60-20% by weight, it was found that the extent of epoxidation increased by the increasing amount of formic acid at a given peroxide concentration. But at high solid content, coagulation of the latex tend occurred. However, it was agreed that higher epoxidation rates could be obtained at higher latex concentration.

Epoxidation of low molecular weight polydiene was usually done in solution by dissolving low molecular weight polymer in organic solvent and using organic peroxy acid. The epoxidation reaction in aqueous phase would be beneficial in easy manipulation, low cost and less toxic. IRAP prepared epoxidised liquid natural rubber (ELNR) by oxidative degradation of natural rubber latex into LNR then continuously epoxidise of LNR with in situ performic acid as shown below:



NR latex m < n epoxidised LNR

The obtained ELNR was simply characterised by spectroscopic method. $^1H$ NMR spectrum showed a peak at 2-3 ppm characteristic of C-H band of epoxide ring. The presence of epoxide group on isoprenic rubber could be confirmed by the absorption peak at 870 and 1240 $cm^{-1}$ of epoxide group in IR spectrum.

Addition reaction between epoxy resins and acrylic acid as a photosensitive molecule had been widely studied.[2,20] T. Nishidubo[14] had used technical grade epoxy resins such as bisphenol type, propylene glycol type and phthalic acid ester type. The condition of the reaction was carried out at 100-110°C for 2 h by using triethylbenzylammonium chloride as a catalyst and monomethoxy quinone[12,13] as a thermopolymerization inhibitor. They found that the degree of the three resins were 99.9 mole%, 99.4 mole% and 95.3 mole%, respectively. The addition reaction of methacrylic acid[17] onto diglycidyl ether of Bisphenol A was also carried at 110°C but using chromium di-isopropyl salicylate as a catalyst.

Polydiene modified by epoxidation reaction was another base molecule having epoxide ring susceptible for fixation of photosensitive acid. The reaction between epoxidised liquid natural rubber and methacrylic acid was studied by using four types of catalysts namely tetramethylammonium methacrylate, potassium hydroxide, pyridine and triphenylphosphine. The condition of the reaction was 100°C at molar ratio [acid]/[epoxide]/[catalyst] = 1:1:0.1 using p-methoxyphenol as an inhibitor. The yield of the addition was 13.3% after 72 h of the reaction by using pyridine. Decker and H-Lexua[18] found that addition reaction of acrylic acid onto epoxidised rubber (ENR) or Epoxidised liquid natural rubber (ELNR) was completed after 16 h by using a large excess of acrylic acid at 35°C.

## MATERIALS AND METHODS

### Material

Natural rubber latex (60% drc) was supplied by Institut de la Recherche Applique sur les Polymeres (IRAP) and by Ansell (Thailand) Co., Ltd.

### Method

### Preparation of liquid natural rubber

A desired amount of natural latex (60% dry rubber content, drc) was diluted to 30% drc in a beaker, then stabilised with 0.3 phr of Vulcastab LW. The latex was stirred at room temperature overnight then transferred to a reaction vessel. After increasing temperature of the latex mixture to 60°C, amount of phenylhydrazine (as listed in Table 1) was added dropwise. Air was passed through the latex at 2-3 l/min. The reaction was allowed to stir at 60°C, for 24 h. At the end of the reaction, water was evaporated by distillation. LNR was then dried under vacuum at 40°C to constant weight. The product obtained was brown viscous liquid and characterized by Infrared spectroscopy, $^1$H NMR spectroscopy. Molecular weight of LNR was determined by viscosity measurement.

### Preparation of epoxidised liquid natural rubber

The liquid natural rubber latex was diluted to 20% drc and the temperature of the latex was decreased to 40°C. After neutralizing the latex with formic acid, a desired amount of formic acid was slowly dropped into the latex and stirred at 40°C for 15 min. The temperature of the latex mixture was again increased to 55°C and 30% $H_2O_2$ were added dropwise. The amount of chemical reagent used in this experiment was shown in Table 2. The reaction was then allowed to stir at 55°C for 48 h. At the end of the reaction, the mixture was neutralized with 30% aqueous sodium hydroxide and then the product was coagulated by heating the latex to 85°C. The ELNR was dried in vacuum at 40°C. The obtained product was brown viscous liquid. IR spectrum, $^1H$ NMR and $^{13}C$ NMR of the ELNR were recorded. Viscosity average molecular weight of ELNR was determined from depolymerization stage of natural rubber latex.

**Molecular weight determination of liquid natural rubber**

Molecular weight of LNR was determined by using viscometric method. The average molecular weight ( $\overline{Mv}$ ) of LNR was calculated from the following equation.

$[\eta] = k\overline{Mv}^a$

$[\eta]$ = Intrinsic viscosity[4]

$k = 50.2 \times 10^{-3}$ ml/g

$a = 0.67$

$[\eta]$ was determined from the intercept of the plot from Huggin equation as follow:

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C$$

$$\ln \eta_r/C = [\eta] + k'[\eta]^2 C$$

$\eta_r$ and $\eta_{sp}$ are relative viscosity and specific viscosity, respectively. They can be determined from efflux times.

$$\eta_r = t/t_0$$

$$\eta_{sp} = \left(\frac{t - t_0}{t_0}\right)$$

$t_0$ = efflux time of pure solvent

$t$ = efflux time of LNR solution at various concentration

Fixation of photosensitive group onto epoxidised liquid natural rubber.

**Preparation of acid-catalyst stock solution**

Stock solution was prepared by mixing catalyst and a photosensitive acid in chloroform at molar ratio of [catalyst*]/[acid**] = 0.1

### Addition reaction of photosensitive acid onto ELNR

ELNR and acid-catalyst stock solution was mixed in chloroform at molar ratio of [acid] : [epoxide] : [catalyst] = 1:1:0.1. The inhibitor, p-methoxyphenol, for homopolymerization was added to the solution at the same mole percent as that of the acid. Total amount of the solution was 60 ml. The mixture was heated at 80-110°C (as desired). Progress of the addition reaction was followed by sampling the solution at different time interval and determined the amount of the residual acid by potentiometric titration with standardised 0.1 M KOH. At the end of the reaction, the modified ELNR was recovered by precipitation in excess methanol. The product obtained was kept in chloroform solution at room temperature in the dark place. The modified product was characterized by FTIR spectroscopy.

### Photocrosslinking reaction of the modified ELNR

The modified ELNR was dissolved in chloroform at 5, 10, 15 and 20% solution. Then it was cast on NaCl support by using coater. After evaporation of the solvent, the film was obtained. The thickness of the film was determined from concentration of sample and type of coater. Thus four different films of approximately 2.5, 5, 7.5 and 10 µm thick were obtained. The film irradiated by ultraviolet radiation.

The evolution of photoreaction was followed by IR spectroscopy in the case of ELNR modified by cinnamic acid. The decrease of C = C of cinnamate at 1,637 $cm^{-1}$ was notified.

## RESULTS AND DISCUSSION

### Preparation of liquid natural rubber (LNR)

LNR was prepared by oxidative degradation reaction using $O_2$ and phenyhydrazine system in the latex phase. As mentioned in previous work[11], the factors that influence on molecular weight of LNR were amount of air flow, phenylhydrazine concentration, reaction time, temperature of the reaction, nonrubber constituents, and metal ions.

In this work, all parameters were fixed except the amount of phenylhydrazine in order to understand the relation of the amount of phenylhydrazine and molecular weight of LNR and to be able to get a desired range of the molecular weight of LNR for the benefit of further reaction.

Two hundred ml of concentrated natural rubber latex was used as starting material for

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* Catalysts used were Benzyltrimethylammonium chloride and pyridine.

** Photopolymerizable acids used were acrylic acid, methacrylic acid and cinnamic acid.

degradation reaction. 0.71-4.07 × $10^{-1}$ moles phenylhydrazine was added and the reaction was carried out at 60°C for 24 h. After evaporation of the water, LNR was obtained and its molecular weight was determined by viscosity measurement, using toluene as the solvent at 25°C. The results are shown in Table 3.

The obtained LNR was brown viscous liquid. The plot of $\overline{M}v$ versus number of mole $\phi NHNH_2$ employed in the reaction, (Figure 1) showed that the extent of oxidative degradation depended on the amount of phenylhydrazine but the rate was nonlinear. The $\overline{M}v$ of LNR obtained decreased with increasing amount of $\phi$ $NHNH_2$.

The results of IR spectroscopy of the prepared LNR listed in Table 4, which showed absorption band at 1,660 $cm^{-1}$, the characteristic of carbon-carbon double bond. There were low intensity absorption bands at 3,300 $cm^{-1}$ and around 1,700 $cm^{-1}$ representing some hydroxy group and carbonyl function, respectively. $^{1}H$ NMR spectrum showed carbon-carbon double bond at 5.14 ppm (Table 5).

## Preparation of epoxidised liquid natural rubber (ELNR)

The obtained ELNR product was brown viscous liquid. It had previously been summarized that chain scission of the polyisoprene molecules did not take place during the epoxidation reaction[9]. In the present study, ELNR similar assumption was made. Therefore the molecular weights of ELNR were taken to the same as those of the starting LNR and the results are shown in Table 6.

The prepared ELNR was characterized by spectroscopic methods, namely:

- IR spectroscopy; The characteristic absorption bands of epoxide group was found at 870 $cm^{-1}$ and 1,240 $cm^{-1}$. Since the olefinic band at 835 $cm^{-1}$ was also detected, the result indicated that epoxidation of LNR was not 100% complete.
- $^{1}H$ NMR spectroscopy; The spectra showed the decrease of olefin proton peak at 5.14 ppm and the appearance of the methine resonance at 2.70 ppm due to the proton attached to the oxirane ring.
- $^{13}C$ NMR spectroscopy; The spectra showed the characteristic chemical shift of the olefin resonances at approximately 125 ppm and that of the oxirane carbon at 64.5 ppm.

## Determination of epoxide content

### Investigation on method for determination of epoxide content

It was found that the determination of ELNR could be done by several methods in order to find the best method suitable for this work. Several trials were first carried out by using ELNR form IRAP, symbolized as ELNR (F) which has $\overline{M}v$ = 10,400 and epoxide content of 27%.

- By infrared spectroscopy; ELNR (F) was cast as a film on NaCl cell and the IR spectra were carried out. The characteristic band of epoxide group was shown at 870 $cm^{-1}$ and that of olefinic band was at 835 $cm^{-1}$. As the absorptivity of the two bands were different, it was not possible to calculate epoxy content by absorbance ratio of 870 and 835 $cm^{-1}$.

- By $^1H$ NMR spectroscopy; ELNR (F) was dissolved in $CDCl_3$ and the $^1H$ NMR spectra were recorded. This spectrum showed that the epoxidation level lead to the decrease of olefinic protons at 5.14 ppm, $(-\overset{|}{C}=CH)$ and the appearance of methine resonance at 2.70 ppm, (CH-O) due to the proton attached to oxirane ring. Due to the occurrence of methine resonance at this resolution, epoxy content was determined by the ratio of the integrated areas of the olefinic and epoxy methine protons, thus the epoxidation level was calculated by the relationship :

$$\text{mole percent of epoxide} = 100\left(\frac{A_{2.70}}{A_{5.14} + A_{2.70}}\right)$$

$A_{2.70}$ and $A_{5.14}$ were integrated area of proton attached to epoxide ring and proton attached to C-C double bonds, respectively, the 28% epoxidation level of ELNR (F) was found.

- by $^{13}C$ NMR spectroscopy; $^{13}C$ NMR spectra were obtained from ELNR (F) dissolved in $CDCl_3$. The epoxy content was determined from the peaks at 125 ppm due to olefinic resonance and at 64.5 ppm due to oxirane carbon. The ratio of the areas of these peaks were used to estimate the quantity of epoxy group compared to the oxirane groups from the following equation:

$$\text{mole percent of epoxide} = 100\left(\frac{A_{64.5}}{A_{64.5} + A_{124.2,\ 125.0,\ 125.7}}\right)$$

The 30% epoxidation was found.

- By titration method; The epoxidation level can be determined from the following equation[21]:

The weight of oxygen (mg) = 1.6 $\Delta T$

$\Delta T$ was the difference of the volume in $cm^3$ of 0.1 M NaOH used to titrate the control and the sample. By this method, 14% of epoxide content was obtained.

ELNR (F) received from IRAP contained 27% epoxide content. It was determined from a calibration curve obtained by using both $^1H$ NMR and IR spectroscopic methods. Table 7 shows epoxide content determined in the present study by different methods. It was found that epoxide content obtained by $^{13}C$ NMR, $^1H$ NMR spectroscopy were closed to the value of ELNR (F) obtained from IRAP.[6,16]

In the case of titration method, only 14% of epoxide content was obtained. The error of titration method might be due to the furanisation occurring during the addition of acid. Therefore a part of epoxide groups were reacted with the acid.

In this work, $^1H$ NMR and $^{13}C$ NMR techniques were considered to be the most suitable methods for the determination of epoxide groups. But from the previous work, it had been known that the error from $^1H$ NMR and $^{13}C$ NMR measurements were about +1.5% and +0.8% respectively. It was evident that $^{13}C$ NMR spectroscopy was the most suitable method for determination of epoxide content in this work.

## Analysis of epoxide content of ELNR

Two prepared samples of ELNR were conducted to the analysis of epoxide content by means of $^{13}C$ NMR spectroscopy. Table 8 shows the epoxide content of ELNRs of the present study.

## Fixation of photosensitive acid onto epoxidised liquid natural rubber

The objective of this reaction was to graft unsaturated carboxylic acid onto epoxide rings on the chain of ELNR via eposide ring.

In this work acrylic acid, methacrylic acid and cinnamic acid were chosen. It was known that these acids had been widely employed in autocurable polymer system because they had good ability in absorption of UV energy. In the first stage, fixation of the three acids onto ELNR (F) were tried, then different parameters of the fixation reaction of acids onto ELNR (F) sample, such as catalysts and temperature of the reaction were investigated. After that, the optimum condition was taken for the fixation reaction of photosensitive acids onto ELNR-1 and ELNR-2 starting material.

## Addition of photosensitive acid onto ELNR (F)

- Addition of cinnamic acid onto ELNR (F); The completion of the reaction took over 80 h. The cinnamic function grafted onto ELNR (F), symbolized as C-ELNR (F) was recovered as viscous brown liquid and light-sensitive, it could undergo photocrosslinking reaction when exposed to the light. C-ELNR (F) was therefore kept in chloroform in the dark place. Percent conversion of the reaction calculated from the residual acid concentration obtained from titration was 16%.

- Addition of methacrylic acid onto ELNR (F); After 80 h the modified product from this reaction symbolised as M-ELNR (F) was recovered. The M-ELNR (F) was partially soluble in chloroform. It showed that some photocrosslinking was occurred. Methacrylic function grafted on ELNR (F) was therefore more light-sensitive than C-ELNR (F). Percent conversion of the reaction was 18.

- Addition of acrylic acid onto ELNR (F); After 80 h, the modified product from this reaction represented by A-ELNR (F) was obtained and kept in chloroform solution in the dark place but it was light-sensitive and could be kept for a few days. Percent conversion of the reaction was 18.

## Characterization of the addition products

The modified ELNR (F) was characterized by IR spectroscopy. The results are shown in Table 9. IR spectrum of the products showed the appearances of carbonyl peaks at 1,726 cm$^{-1}$ for cinnamate groups, 1,728 cm$^{-1}$ for acrylate groups, and 1,720 cm$^{-1}$ for methacrylate groups. Besides the C=O stretching peak, the photosensitive rubber that reacted with cinnamic acid also showed C=C stretching vibration of cinnamate group at 1,637 cm$^{-1}$, and = $CH_2$ deformation at 1,408 cm$^{-1}$ of acrylate group.

## Photocrosslinking of modified ELNR by ultraviolet (UV) irradiation

It was well known that under UV irradiation the cinnamic function could undergo photodimerization which was dued to the reaction between two carbon-carbon double bonds. The IR spectrum of the sample showed that decrease of carbon-carbon double bonds absorption at 1,637 cm$^{-1}$ the mechanism of the photocrosslinking of the photosensitive elastomers could be presented as the reaction between carbon - carbon double bonds of cinnamate function.[7]

## Kinetic studies of photocrosslinking reaction

Prepared ELNRs containing cinnamate functions were used to study the kinetic of photocrosslinking under UV irradiation. C-ELNR-1-9, C-ELNR-2-7 and C-ELNR (F)-7 contain 9, 7, and 7% fixation of cinnamate function on its chain, respectively. Each of these sample dissolved in 15% chloroform solution was cast on NaCl cell with the aid of a 50 µm with wire bar coater. After evaporation of the solvent, solid film was obtained. The thickness of the film was calculated from the sample concentration and type of wire bar coater, thus a film of 7.5 µm was obtained. The film of photosensitive elastomer was placed under 10 W mercury lamp (at the distance of 10 cm) for UV irradiation at different times. By using IR spectroscopy, an absorption band at 1,637 cm$^{-1}$ due to carbon-carbon double bonds of cinnamate group of each sample was followed. Percent conversion of crosslinking reaction was determined by the following equation:

$$\%\ \text{conversion} = \frac{A_t - A_0}{A_0} \times 100$$

$A_t$ = Absorbance of carbon-carbon double bonds at irradiation time t

$A_0$ = Absorbance of carbon-carbon double bond at irradiation time 0

It was found that the rate of photocrosslinking was fast at first. The progress of photocrosslinking was decreased at longer time and the reaction was not 100%. This might be due to the fact that the reaction was carried out in solid state, after partial crosslinking the molecular chain was fixed, therefore the possibility of cinnamate functions to move close each other was less effective.

C-ELNR-1-9 had slightly higher rate of photocrosslinking reaction. This might be due to its lowest molecular weight among the three samples. However the rate of photocrosslinking was not much different. Considering that the molecular weights of ELNR-1, ELNR (F) and ELNR-2 were 7,000, 10,400 and 23,000 respectively, it might be concluded that molecular weight of ELNR had little effect on the rate of photocrosslinking.

In case of the amounts of cinnamate functions fixed on the elastomeric chain, it was found that 7% or 9% of cinnamate group had slightly effect on the rate of photocrosslinking. The irradiation time for complete crosslinking was quite long (100 min). This might be because of low intensity light source used.

### Effect of film thickness on the rate of photocrosslinking reaction

This effect was carried out in order to study the effect of thickness of coated film on the rate of photocuring. The photocrosslinking reaction was carried out with ELNR (F)-11.

Film specimen for UV-irradiation was prepared by coating on NaCl cell for infrared analyses. Different film thicknesses were prepared including 2.5, 5, 7.5 and 10 μm. UV irradiation was carried out at room temperature at the distance of 4 cm from a mercury lamp (10 W). The photocrosslinking rate of cinnamate group was determined by the intensity change of the infrared absorption at 1,637 $cm^{-1}$ due to carbon-carbon double bond of cinnamate group by using FTIR spectroscopy. The results were shown in Figure 2.

The result showed that, at first the rate of crosslinking was high but the slope decreased with photocrosslinking time. Almost 100% of photocrosslink reaction was obtained with 2.5 μm thickness of film sample. But only 60% of photocrosslinking was obtained in the case of 10 μm thickness of film sample. It was evident that by using the same source of UV irradiation, the thinner of the sample was more effective than the thicker one because the photocrosslinking was occurred at film's surface.

## CONCLUSION

Epoxidised liquid natural rubber (ELNR) could be prepared by epoxidation of depolymerized natural rubber latex with in situ performic acid. The reaction procedure was carried out by preparing depolymerized natural rubber in latex phase using redox system of phenylhydrazine and oxygen then epoxidation reaction was achieved by addition of formic acid and hydrogen peroxide.

Determination of epoxide content on ELNR was obtained by the aid of $^{13}C$ NMR spectroscopy.

Cinnamic, methacrylic, and acrylic acids were used as photosensitive acids to fix onto ELNR via epoxide ring. It was found that the addition reaction of cinnamic acid was slower than methacrylic acid and acrylic acid. This might be due to the steric effect of bulky phenyl group so it had less mobility than the others.

Photocrosslinking of ELNR containing cinnamate group was carried out as solid film on NaCl support under UV irradiation. It was found that the rate of photocrosslinking depended on percentage of photosensitive groups, film's thickness and molecular weight of elastomers.

## REFERENCES

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**Table 1. Amount of phenylhydrazine used in this experiment**

| Experiment number | Amount of latex (ml) | Amount of $\phi$ NHNH$_2$ (x10$^{-1}$) (mole) |
|---|---|---|
| 1 | 200 | 4.07 |
| 2 | 200 | 3.56 |
| 3 | 200 | 2.75 |
| 4 | 200 | 1.53 |
| 5 | 200 | 1.01 |
| 6 | 200 | 0.71 |

**Table 2. Volume of chemical reagent used in preparation of ELNR**

| Experiment number | Amount of latex (ml) | $\phi$ NHNH$_2$ (10$^{-1}$) (mole) | HCOOH (10$^{-1}$) (mole) | $H_2O_2$ (10$^{-1}$) (mole) |
|---|---|---|---|---|
| ELNR-1 | 300 | 2.30 | 8.15 | 4.08 |
| ELNR-2 | 300 | 1.53 | 8.15 | 4.08 |

**Table 3. Effect of the amount of phenylhydrazine ($\phi$ NHNH$_2$) on molecular weight ($\overline{M}v$) of LNR**

| Amount of $\phi$ NHNH$_2$ (x10$^{-1}$) (mole) | Molecular weight of LNR ($\overline{M}v$) (x10$^{-3}$) |
|---|---|
| 4.07 | 3.4 |
| 3.56 | 4.0 |
| 2.75 | 7.1 |
| 1.53 | 8.2 |
| 1.01 | 10.6 |
| 0.71 | 19.5 |

**Table 4. Significant IR absorption bands of LNR**

| Vibration | $\gamma$ (cm$^{-1}$) |
|---|---|
| =C-H stretching | 3,028 |
| C-H stretching | |
| $CH_3$ | 2,960, 2,870 |
| $CH_2$ | 2,925, 2,850 |
| C-H bending | |
| $CH_3$ | 1,375 |
| $CH_2$ | 1,465 |
| C-H wagging | 835 |
| C=C stretching | 1,660 |
| hydroxy group | 3,300 |
| carbonyl group | 1,700 |

**Table 5. Data from $^1H$ NMR spectrum of LNR**

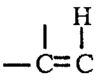
| Proton | Chemical shift ($\delta$) (ppm) |
|---|---|
| $-CH_2$ and $-CH_3$ | 1-2.5 |
|  $-\overset{|}{C}=\overset{\overset{H}{|}}{C}$ | 5.14 |

**Table 6. Experimental data of molecular weight of prepared ELNR estimated from LNR molecules**

| Experiment number | Molecular weight ($\overline{Mv}$) |
|---|---|
| ELNR-1 | 7,000 |
| ELNR-2 | 23,000 |

Table 7. **Data of epoxy content determined by different methods**

| Method | IRAP | $^{1}$H NMR | $^{13}$C NMR | Titration |
|---|---|---|---|---|
| % epoxide content | 27 | 28 | 20 | 14 |

Table 8. **Data of epoxide content determined by $^{13}$C NMR spectroscopy**

| Experiment number | $H_2O_2$ (mole) | Formic acid (mole) | Epoxide content (%) |
|---|---|---|---|
| ELNR-1 | 0.8157 | 0.4079 | 20 |
| ELNR-2 | 0.8157 | 0.4079 | 18 |
| ELNR(F) | - | - | 27[a] |

a = reported by IRAP

Table 9. **IR absorption of carboxylated liquid natural rubber**

| Vibration | $\gamma$(cm$^{-1}$) |
|---|---|
| O-H stretching | 3,500 |
| C=O stretching of |  |
| acrylate groups | 1,728 |
| methacrylate groups | 1,720 |
| cinnamate groups | 1,726 |
| C=C stretching of cinnamate groups | 1,637 |
| $=CH_2$ deformation of acrylate groups | 1,408 |
| =C rocking of cinnamate and acrylate groups | 1,280 |
| $=CH_2$ wagging of acrylate groups | 970 |

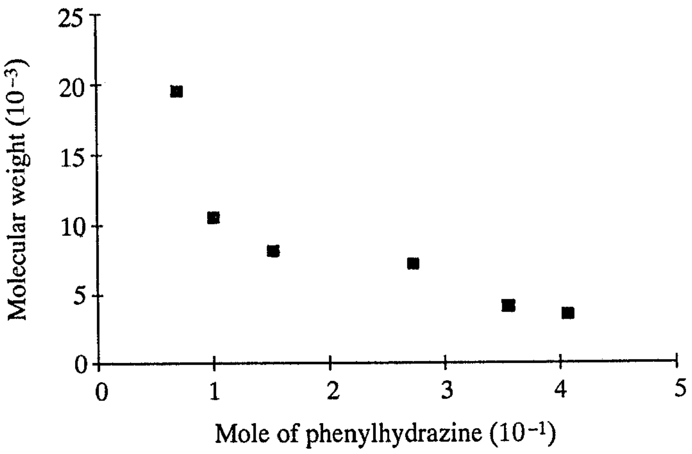


**Fig. 1 Plot of the phenylhydrazine concentration and molecular weight ($\overline{Mv}$) of LNR**

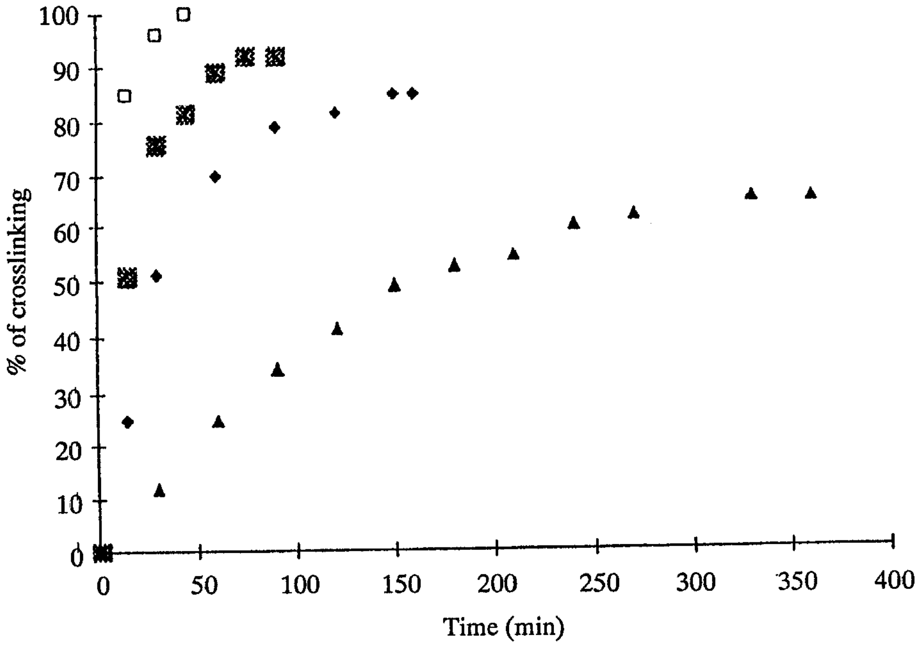


**Fig. 2 Plot of % crosslinking by UV irradiation of different ELNR thickness and % concentration of ELNR solution (w/v) (light intensity: 13.4 × $10^2$ μw/$cm^2$) (□ 2.5 μm, ▨ 5 μm, ◆ 7.5 μm, ▲ 10 μm)**