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Partial conversion of epoxide groups to diols in epoxidized natural rubber

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Epoxidized natural rubber (ENR) is fairly stable in its latex state. Only a small amount of the epoxide groups were converted to diols when the latex was boiled under mildly acidic or alkaline pH. Although the small amount of diols could not be determined accurately by ^{1}H nuclear magnetic resonance (n.m.r.), their presence could be demonstrated by the degradation reaction using lead tetraacetate. The formation of –OH and carbonyl groups after the degradation could be clearly seen in the infra-red spectra. Higher level of diols could be introduced by reacting ENR-50 dissolved in toluene with a mixture containing water and acetic acid in tetrahydrofuran at 60°C. The amount of conversion of epoxide to diol increases with reaction time, and up to 23 mol% of diol in the rubber chain can be achieved after 24 h of reaction. The extent of conversion can be determined from the ^{1}H n.m.r. spectra of the samples. The ENR containing diols in the main chain could serve as a good intermediate for further chemical modifications. For example, cleavage of the diol groups with specific reagents could offer a convenient route to the production of liquid ENR. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: epoxidized natural rubber; conversion to diols; degradation)

INTRODUCTION

Chemical modification of natural rubber (NR) has frequently been attempted with two objectives: to improve the performance of NR in specific application, and to convert NR into a new material which could diversify the traditional uses of natural rubber (NR). Epoxidation represents a particularly attractive and convenient method for transforming NR into a new polymer with certain interesting properties. NR has variously been epoxidized in solution by perbenzoic[1], perpthallic[2,3], and peracetic[4,5] acids. Due to the different reaction conditions, there were some conflicting results on the properties of the products. For instance, one patent[6] claimed that epoxidation improved the solvent resistance and tensile strength of the polymers, whereas other workers have reported a reduction in tensile strength and mechanical properties[2,7].

There is obvious economic incentive to conduct the epoxidation of NR in latex, so as to minimize processing and solvent costs. It is only recently that efficient epoxidation of NR in latex to high modification levels has been realized. The reaction can be readily carried out by peracid, generated from the reaction of formic acid and hydrogen peroxide, on the rubber at the latex stage[8,9] to result in a random distribution of epoxide groups along the polymer backbone. Currently two forms of this material, epoxidized natural rubber (ENR)-25 (25 mol% epoxidized) and ENR-50 (50 mol% epoxidized) are commercially produced in Malaysia. The general properties of these materials have been reported previously[10]. Substantial physical property changes occur with increasing level of epoxidation; thus, as the level of epoxidation goes up the glass transition temperature (T_g) increases, oil resistance increases and gas permeability decreases. ENR-50 has oil resistance and air permeability comparable to some of the speciality synthetic elastomers such as chloroprene and butyl rubbers. In addition, ENR can undergo strain crystallization[11] like natural rubber and hence has superior tensile and fatigue properties. Epoxidation renders the polymer highly polar, which enable ready compatibility of, for example ENR with PVC[12], nylon[13] and carboxylated nitrile rubber[14].

ENR contains both epoxide and unsaturated sites. While the double bonds can be crosslinked by sulfur and peroxide, the epoxide groups provide alternative sites for crosslinking with other polyfunctional chemicals[15] such as dibasic acids[16] and polyamines[17]. Besides, the epoxide group can also serve as the site for further chemical modification through its reactions with various monofunctional chemicals. For example, the reaction of ENR with benzoic acid has led to a significant increase in T_g of the material, the increase being proportional to the amount of incorporated benzoic acid[18].

This paper reports the partial ring-opening of ENR-50 by hydrolysis of the epoxide groups to generate some diols in the polymer chains. The amount of ring-opening can be analysed by ^{1}H nuclear magnetic resonance spectroscopy (n.m.r.).

EXPERIMENTAL

Materials

Freshly prepared samples of ENR-50, both in latex and dry rubber forms, were kind gifts from Guthrie Research Chemara, and were nominally of 50 mol% epoxide composition. All other chemicals were used as commercially supplied.

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Hydrolysis of ENR-50 in latex

ENR-50 latex (20 ml) was diluted to 150 ml with distilled water. The mixture was adjusted to the specified pH with the addition of dilute acidic acid (5%) or NaOH solution (1 M). The mixture was heated to boiling where the rubber coagulated out after 30 min. The rubber was washed under running water, pressed into a thin sheet and dried in a vacuum oven at room temperature. To further purify the rubber, the sample was dissolved in toluene (2 g/100 ml) and reprecipitated in excess methanol. The rubber was then dried in a vacuum oven at room temperature and kept in a desiccator under nitrogen atmosphere before analysis.

Degradation of the hydrolysed rubber

The procedure was a modification of a method described previously[19]. Thus 0.5 g of the hydrolysed ENR-50 was dissolved in 50 ml toluene. To this was then added 5.0 ml of a 0.04 M solution of $Pb(OAc)_4$ in glacial acetic acid. After mixing, the flask was immersed in a water bath set at 30°C and allowed to react for 60 min. The rubber was precipitated by adding 200 ml of methanol. The rubber was isolated, washed with methanol and dried in a vacuum oven at room temperature.

Viscosity measurement

Viscosity measurements were made on approximately $0.1\,g\,dl^{-1}$ solutions of rubber samples in toluene at $30.00 \pm 0.02°C$. A capillary Ubbelohde viscometer was used and dilution of the polymer solution was conveniently carried out by adding a known amount of toluene directly into the viscometer.

Hydrolysis of ENR-50 in toluene solution

About 20 g of ENR-50 was milled into a flat sheet on a laboratory two-roll mill at room temperature. It was cut into small strips and put into a stopper conical flask containing 100 ml toluene and a Teflon-coated magnetic stirrer bar. The rubber was allowed to dissolve completely after being stirred with a magnetic stirrer overnight. The rubber solution was treated with a mixture of 80 ml tetrahydrofuran (THF), 15 ml distilled water and 5 ml acetic acid. The reaction flask was put into a water bath set at 60°C and stirred with a submersion magnetic stirrer. After the specified reaction time, 20 ml of the solution was taken, and the rubber precipitated into 150 ml methanol. The rubber was then dried in a vacuum oven and kept in a desiccator under nitrogen atmosphere before analysis.

Characterization of modified products

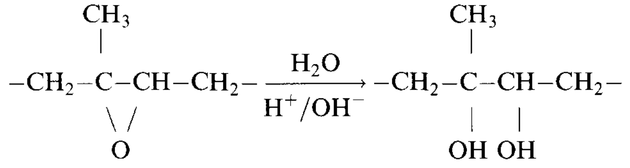
The ^1H n.m.r. spectra of the rubber samples in $CDCl_3$ solution (3% w/v) were recorded on a JEOL JNM-GSX 270 Fourier transform (*FT*) n.m.r. spectrometer at 27°C. Films of rubbers were cast on sodium chloride cells and the infra-red (i.r.) spectra recorded on a Perkin Elmer *FT* i.r. 1600 instrument.

RESULTS AND DISCUSSION

Generally, the epoxide groups of ENR are not reactive to nucleophilic reagents under ambient conditions[20]. Reaction of the dry rubber with organic acids could only occur at elevated temperatures[16,18]. However, it has been reported that ENR in organic solvent treated with aluminum isopropoxide could generate the corresponding allylic alcohol[21], and when treated with lithium aluminum hydride could produce a nonallylic hydroxyl group[22]. Direct treatment of ENR-50 in toluene with strong acid has led to various side reactions such as crosslinking and cyclization.

Ring-opening in ENR latex

According to the supplier of the latex sample, alkali was normally added to neutralize the excess formic and performic acid after the epoxidation of NR latex. The latex has also been stabilized by the addition of a small amount of polyethylene oxide. Unlike NR latex, the rubber could not be coagulated at room temperature by the addition of acid into the ENR latex. The rubber was normally isolated by passing steam into the latex. In our current works, we found that the ENR latex could be slightly hydrolysed under mildly acidic (pH 5) or alkaline (pH 11) conditions to diols by boiling the diluted latex for more than 30 min, when all the rubber coagulated out of the latex.



$$-CH_2-\underset{O}{\underset{\backslash\ \ /}{\overset{CH_3}{\overset{|}{C}}-CH}}-CH_2- \xrightarrow[H^+/OH^-]{H_2O} -CH_2-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{OH}{\underset{|}{CH}}-CH_2- \qquad (1)$$

Although ^1H n.m.r. of the hydrolysed rubber showed the presence of a very small peak at 3.47 ppm due to the diol groups, it was difficult to determine the amount accurately. The presence of such diol groups along the main chain of the ENR could be further demonstrated by the reaction with $Pb(OAc)_4$ described previously[19]. *Figure 1* shows the i.r. spectra of the hydrolysed rubbers isolated after the degradation reaction. Besides the broad peak at $3500\,cm^{-1}$ due to –OH, another peak appeared

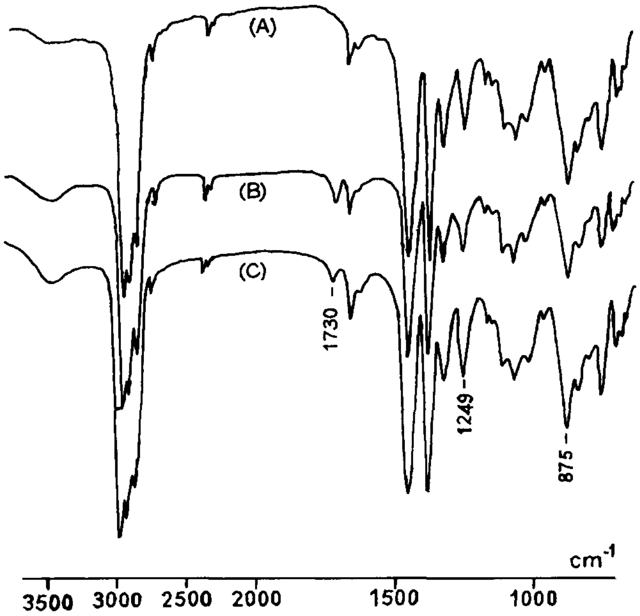
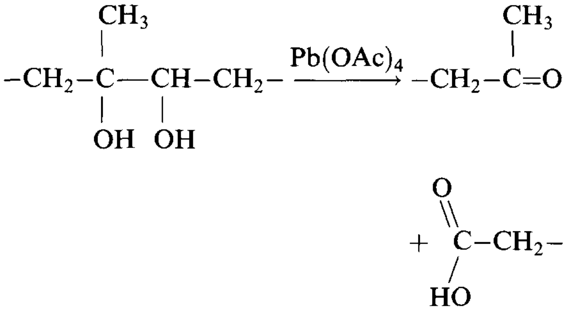


Figure 1 *FT* i.r. spectra of the control sample (A), and after the degradation with $Pb(OAc)_4$ of the rubber isolated from the ENR latex boiled at pH 5 (B) and at pH 11 (C)

around 1730 cm^{-1}, which indicated the presence of carbonyl groups generated during the chain scission reactions.



$$-CH_2-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_2- \xrightarrow{Pb(OAc)_4} -CH_2-\overset{CH_3}{C}=O + \underset{HO}{\overset{O}{C}}-CH_2- \quad (2)$$

The other parts of the spectra, particularly the peaks at 875 and 1249 cm^{-1} (due to epoxide groups) were more or less similar, indicating that only a very small amount of the epoxide groups were ring-opened.

Degradation of diol groups on the main chain of the polymer would lead to a decrease in molecular weight. This was supported by the viscometry measurements of the samples (*Table 1*) which show a significant drop in intrinsic viscosity of the rubber after reacting with $Pb(OAc)_4$.

Table 1 Viscometry measurements of rubbers before and after degradation with lead tetraacetate

	$[\eta]$ (g dl^{-1})	
Sample	Initial	After degradation
Control	2.51	2.20
Hydrolysed at pH 5	2.13	1.54
Hydrolysed at pH 11	2.10	1.66

Control sample is the rubber isolated by boiling the initial ENR-50 latex at pH 8

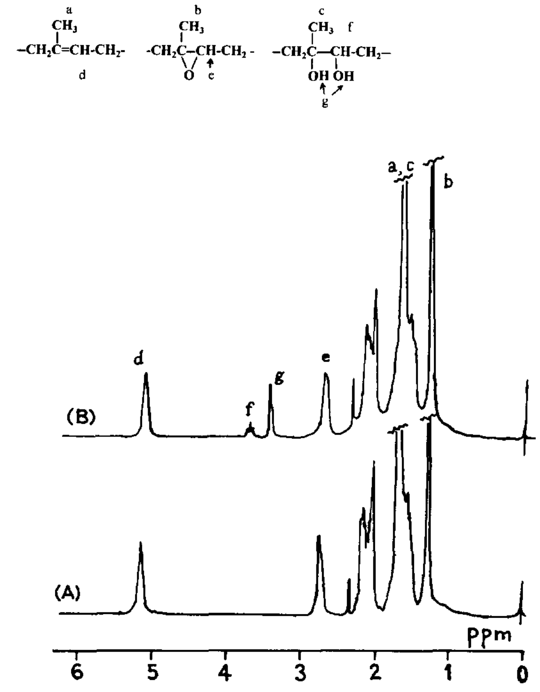


Figure 2 ^{1}H n.m.r. spectra of the initial ENR-50 (A) and one of the partially hydrolysed samples (B)

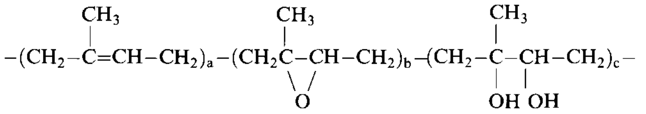
Table 2 Hydrolysis of epoxide groups in ENR-50

Reaction time (h)	mol% of the unit in the chemically modified polymer		
	C=C	Epoxide	Diol
Control	45.8	54.1	0.0
2	45.6	48.1	6.2
4	44.8	46.0	9.2
24	44.4	33.0	22.7

Based on calculations from ^{1}H n.m.r. spectrum of each sample

Ring-opening reaction in organic solvent

On the other hand, a greater amount of ring-opening to diols occurred when the ENR-50 dissolved in toluene was treated with a mixture of THF, water and acetic acid, even at a lower temperature of 60°C. The extent of the conversion increases with reaction time, and can be calculated from the ^{1}H n.m.r. spectra of the samples as shown in *Figure 2*. The ^{1}H n.m.r. spectrum of ENR-50 was consistent with the published data on ENR[23]. The structure of a partially ring-opened ENR-50 can be represented as follows:



$$-(CH_2-\overset{CH_3}{C}=CH-CH_2)_a-(CH_2\underset{O}{\overset{CH_3}{C}-CH}-CH_2)_b-(CH_2-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_2)_c-$$

where a, b and c represent the numbers of the respective units in the polymer chain. The vinylic proton of the isoprene unit was at around 5.1 ppm. As the C=C double bond was converted to the highly strained cyclic epoxide unit, the tertiary proton on the epoxide ring was shifted to 2.7 ppm. These two hydrogen peaks have been widely employed to determine the degree of epoxidation[23,24]. As the epoxide was ring-opened to the diol structure, the same tertiary proton has a lower field shift to 3.74 ppm. It can be seen as a triplet due to the coupling effect of the adjacent $-CH_2-$. The $-OH$ of the diols was detected at 3.47 ppm. These peaks, together with those at 5.1 and 2.7 ppm could be used to determine the amount of C=C double bonds, epoxide groups and diols in the partially hydrolysed ENR-50 samples. The results are summarized in *Table 2*. The amount of conversion of epoxide groups to diols increases with reaction time.

CONCLUSION

The degradation of acid hydrolysed epoxidized synthetic rubber by both lead tetraacetate and periodic acid have been reported[19], however, the extent of conversion of epoxide to diol was not determined. The present investigation has shown that the ENR-50 latex was fairly stable toward hydrolysis at neutral pH. Only a small amount of ring opening could occur when the latex was boiled at either mildly acidic or alkali conditions. A greater and more controlled amount of conversion of epoxide groups to diols may be achieved by treating ENR-50 dissolved in toluene with a mixture containing water, acetic acid and THF. The extent of conversion can be calculated from the ^{1}H n.m.r. spectra of the samples. The degradation of these partially hydrolysed ENR-50 rubber through cleavage of the diol groups with specific reagents such as those mentioned earlier[19] could offer a route to the production of liquid ENR.

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