

On the Stability and *In Situ* Epoxidation of Natural Rubber in Latex by Performic Acid

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SYNOPSIS

The aggregative stability of natural rubber (NR) latex stabilized by nonionic, fatty alcohol ethylene oxide condensate surfactant (Verol S-15) was studied in the presence of formic acid. Natural rubber latex having an additional 3–5 phr surfactant is stable at pH 2 when acidified by formic acid and can be successfully subjected to the subsequent *in situ* epoxidation. Using a large ratio of H₂O₂ to isoprene unit (0.4–4.0 M/M) and large excess of H₂O₂ to HCOOH (3–13 M/M) in reaction, the *in situ* epoxidation can be performed with reaction mixture having dry rubber content up to 35–37% at room temperature or up to 28% at 50°C. This reaction leads to products of large range of epoxide contents and characterized by absence of side-ring opening groups, proved by IR and ¹H-NMR analysis. By infrared spectroscopy it was demonstrated a good correlation between the absorbances of the residual double bonds and of the epoxide groups versus the epoxide content in the range from 0 to approx. 60 mol % level. The solubility and gel content were studied in various solvents, demonstrating that epoxidation leads to increasing gel content at high epoxide levels and to enhancing sensitivity of the product toward polar solvents. By GPC, it was shown for the soluble fraction that epoxidation was accompanied by reducing the molecular weight and by change of the MWD compared with the original NR.

INTRODUCTION

The epoxidation of natural rubber (NR) can be performed both by *in situ* or preformed peracids.¹ The *in situ* epoxidation can be applied to NR existing in different physical states such as in solution,^{2,3} in thin solid sheets⁴ or in latex.⁵ In 1981, in one of the first paper in this field, the *in situ* formed performic acid was used to epoxidize NR in latex.⁶ The reaction was carried out using latex without additional surfactant and led to very limited epoxide content (approx. 6–7 mol %). In recent years, the *in situ* epoxidation was also studied for latexes stabilized by cationic surfactant⁷ or by nonionic surfactants.⁸

In spite of many papers published in this field, up to now there has been no paper dealing with the

study of both the stability of NR latex and subsequent process of its epoxidation. The aggregative stability is of great importance and is in close correlation with the success of the epoxidation. This problem needs special attention whenever the chemical transformation of NR latex is performed in acidic medium or by using acidic reagents. On the other hand, up to now, this reaction has been studied in a rather low range of dry rubber contents (starting with latexes of 20–30%, in reaction they have effective 8–12% dry rubber content).

In this paper, continuing our study on the aggregative stability and chemical transformation of NR,^{9,10} we investigate the aggregative stability of NR latex in presence of formic acid and subsequent *in situ* epoxidation process using medium to high dry rubber content latexes. The work concerns also the spectral characteristics, solubility, gel content, molecular weight, and MWD of epoxidized natural rubber (ENR) products.

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EXPERIMENTAL

Materials

Natural rubber latex: full ammonia, centrifuged latex of 58% dry rubber content (Qualitex).

Surfactant: Fatty alcohol ethyleneoxide condensate, nonionic class Verol S-15 (Verila, Bulgaria), cloud point of 72–75°C.

Formic acid (p.a) of 98% (Ferak).

Hydrogen peroxide (purum): 30% aqueous solution (Fluka).

All other reagents, solvents and indicators used were of reagent grade and were used as supplied.

Procedure

Method for preparation of the latex system and determination of its aggregative stability was presented in detail in our previous paper.¹¹

***In situ* Epoxidation Procedure.** Nonionic surfactant, Verol S-15, prepared as 20% aqueous solution was introduced (the usual dose was 3–5 phr) into NR latex under continuous stirring. The stabilized latex was stepwise acidified with 50–98% formic acid to pH 2.2–2.5. When the epoxidation was performed at 50°C, the necessary amount of H₂O₂ was slowly dropped for approx. 30 min. The fast introduction of this reagent is not recommended to avoid an excessive development of oxygen due to the decomposition of hydrogen peroxide at high temperature. For epoxidation at room temperature, the dropping process could be reduced to 15–20 min. The first sample was taken immediately after finishing the dropping and the other ones were taken at various time intervals. The reaction duration was between 6 and 14 h at 50°C and from 40 to 120 h at room temperature. After epoxidation, the product was coagulated in 50% aqueous alcohol, filtered, washed with distilled water, soaked in 1–1.5% w/v Na₂CO₃ solution for 24 h, washed again to pH 7, then pressed in a thin sheet (1.5–2 mm), and dried at 40°C under vacuum to constant weight before analysis.

Analysis

The epoxide contents of ENR samples at low level of modification (below 15 mol %) were determined by direct titration with HBr in glacial acetic acid (method of Durbetaki¹²). Higher contents of epoxide groups were determined by ¹H-NMR,¹³ by differential scanning calorimetry (DSC),¹³ and by IRS analysis (the method of Davey et al.¹⁴). The struc-

ture of ENR samples were studied by IRS, using film cast directly from chloroform–methyl ethyl ketone (1/1 v/v) solution on KBr windows or by ¹H-NMR spectra recorded from CDCl₃ solution. The IR and NMR spectra were taken on Specord M-80 (Carl-Zeiss) and on Jeol JNM-PS-100 spectrometer. Tg values were determined by DSC technique, using a Perkin-Elmer DSC-2C apparatus with thermal analysis data station (TADT) supplied by Perkin-Elmer. Gel contents in various solvents were determined at room temperature using a standard method.¹⁵

Molecular weight, polydispersity, and MWD were determined by GPC technique. All the analysis were run in tetrahydrofuran (THF) solution at 45°C on a Waters GPC apparatus equipped with superstyragel columns and R-401 refractive index detector.

RESULTS AND DISCUSSION

Aggregative Stability of NR in the Presence of Formic Acid

The stability of NR latex stabilized by a nonionic surfactant (3–5% of dry rubber) of fatty alcohol ethylene oxide condensate type, Verol S-15, was studied in the presence of formic acid. The acid of various concentration was slowly dropped into latex while the pH values were followed during the acidification process.

Variation of pH of latex system having 27% drc, stabilized by 5 part per hundred of dry rubber (phr) S-15 during this process, using formic acids of different concentrations, is presented in Figure 1. It is seen that, starting from the same dry rubber content (drc) of the original latex, the higher the acidic concentration, the deeper (and faster) is the decrease of the pH values (see Fig. 1, compare curves 1–4 for gradually decreasing formic acid concentrations). The experiments showed that concentrated latex of 45–60% drc, without additional surfactant, readily coagulates on adding concentrated formic acid. By using additional nonionic surfactant, the latex system becomes less sensitive to the variation of pH and its aggregative stability is greatly increased. In our experiments, using 98% formic acid to acidify latexes having from 27 to 54% drc, it could be obtained the final pH 1.8–2.0 without spontaneous coagulation. Depending on the conditions of acidification, the acidified latexes were stable from 5 days to 3 weeks. Formic acid of lower concentration used in higher dose leads to higher final pH and also to a higher aggregative stability (see Table I).

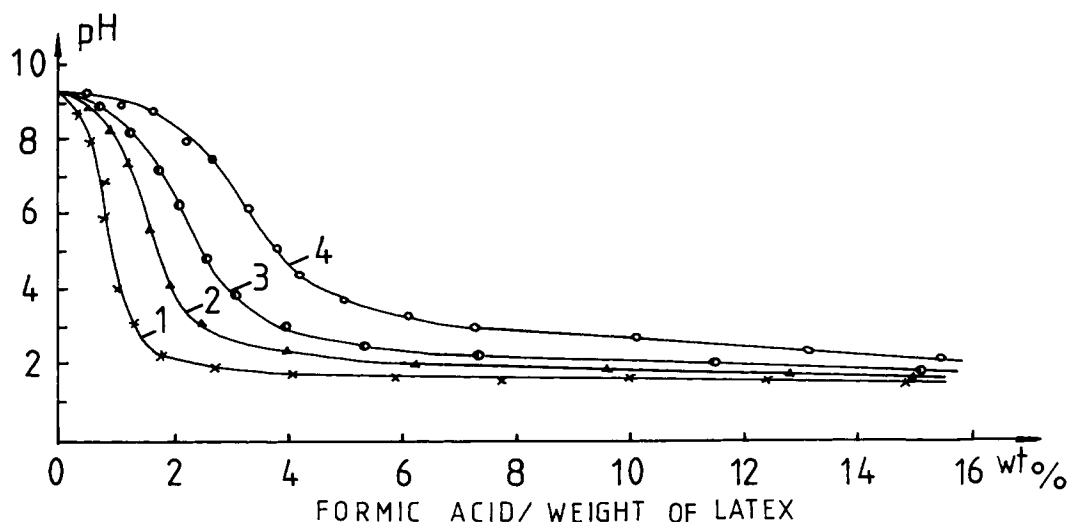


Figure 1 Variation of pH during acidification process in presence of different formic acid concentrations. Conditions: natural rubber latex of 27% dry rubber content, stabilized by 5 phr nonionic surfactant (Verol S-15). Concentration of HCOOH: (1) (×) 98%; (2) (▲) 55%; (3) (●) 36%; (4) (○) 20%.

The stability of latex system depends also on the initial dry rubber content. Figure 2 shows variations of pH values for latex having different drc during acidification by 98% formic acid (Fig. 2, curves 1 and 2). Under this treatment, the more diluted latex (of 12.7% drc) quickly reduced its own pH and attained the final range sooner. It shows also a better stability compared to the concentrated latex (the stability for latexes of 12.7 and 54% drc were 14 and 2 days, respectively).

The latex stabilized by higher concentration of surfactant also shows less sensitivity toward the acid and its pH also decreases with slower rate than the system of lower S-15 content (see Fig. 2, compare curve 3 to 1 and 2, respectively).

Using additional nonionic surfactant, it can obtain stable latex systems of pH approx. 1.0 in the presence of HCl¹¹ but using formic acid, the pH limit usually is approx. 1.8–2.0.

Experiments made with latexes stabilized by 3–5 phr Verol S-15 in large range of dry rubber content (12–58%) showed that all systems of lower dry rubber content (below 20% drc) are stable for weeks to months at pH 1.8–2.0 while those of higher drc are stable only at pH = 2–2.2 if prepared by 50–98% formic acid.

For the epoxidation experiments, we have used latexes of initially high dry rubber content (without preliminary dilution), stabilized by 3–5 phr Verol S-15, acidified by 50% formic acid to pH 2.2–2.5. Under these conditions, NR latexes show good stability and permit the *in situ* epoxidation to be carried out successfully.

***In Situ* Epoxidation of Natural Rubber in Latex**

The early work on the *in situ* epoxidation of NR in latex was performed without using additional sur-

Table I Influence of Formic Acid Concentration on the Final pH and the Aggregative Stability of Natural Rubber Latex^a

HCOOH Conc (%)	HCOOH Dose (M/l)	pH	Aggregative Stability (days)
98	1.59	1.8	5
55	1.96	2.0	8
36	3.02	2.3	11
20	3.35	2.6	22

^a Conditions: Latex of 27% dry rubber content, stabilized by 5 phr Verol S-15, stored in a sealed tube at room temperature.

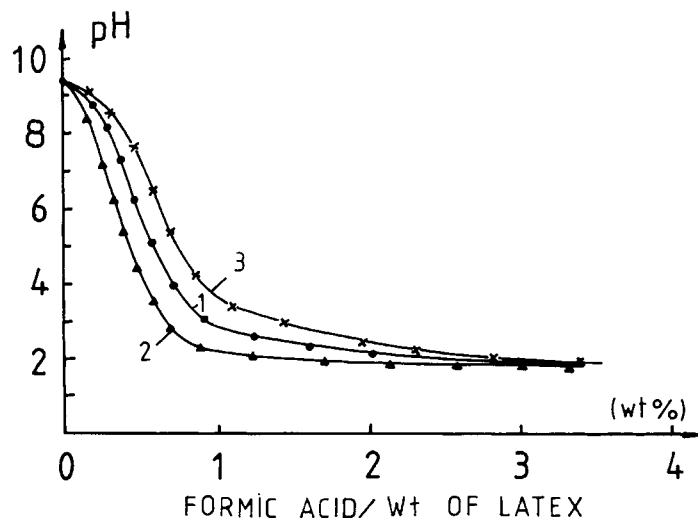


Figure 2 Variation of pH of latex having different dry rubber contents in presence of 98% formic acid. Conditions: (1) (●) 54% drc, 3 phr S-15; (2) (▲) 12.5% drc, 3 phr S-15; (3) (×) 27.5% drc, 5 phr S-15.

factant.⁶ The reaction was carried out to a limited epoxide content and was accompanied by an early coagulation together with large amount of ring-opening products due to very large excess of formic acid used (ratio of $H_2O_2/HCOOH = 0.05-0.27 M/M$). Recently, Perera¹⁶ has studied this reaction by NMR technique in other range of reagent ratio ($H_2O_2/HCOOH = 0.5-3.4 M/M$). All these authors have studied the epoxidation in rather low dry rubber content latexes (starting with 20–30% drc latex, in reaction it has effectively from 7.5 to 12.5% drc; see also Table II).

In the present work, the *in situ* epoxidation was studied for a great majority of systems having higher dry rubber content (concentration of polyisoprene in reaction usually was 28–37%) and great ratio of $H_2O_2/HCOOH$. Except the data from a patent specification,⁸ these conditions are evidently different from the other previous works (see Table II).

The kinetic curves for epoxidation at 50 and 25°C are presented in Figure 3. The reaction proceeds normally under continuous stirring and the conversion of NR to epoxidized natural rubber (ENR) is dependent on the ratio of H_2O_2 to isoprene unit (see

Table II Comparison of Composition of Prepared Latex and Conditions for In Situ Epoxidation ($H_2O_2/HCOOH$ System)

Data	Author					
	Present Paper		Gelling ⁸	Perera ¹⁶	SCNg ⁶	LHGan ⁷
Temperature	50°C	R _T	50–60°C	R _T	30°C	3–25°C
Isoprene unit (M/L)	1.6–4.1	1.6–5.4	1.8–3.5	1.1–1.7	1.85	1.20
H_2O_2/IP (M/M)	1.0–3.9	0.4–3.9	0.74–3.0	1.54	0.26–0.96	1.36
$H_2O_2/acid$ (M/M)	5–13	3.3–13	3.7–10	0.5–3.4	0.05–0.27	0.46
Surfactant (g/L)	5–14	4–18.4	4.2–6.1	13	Not used	Cationic
drc						
Initial	27–58%	58%	30%	20%	30%	24%
In reaction	11–28%	15–37%	12–21%	7.5–11.5%	12.6%	8.2%
pH	2.3–2.5	2–2.5	Nonspec.	Nonspec.	Nonspec.	Nonspec.
Reaction time (h)	12–14	60–120	2.5–24	30–70	10	8–30
Max. epoxide content (mol %)	55–57	70–80	50	90	6.5–7.5	40

^a Nonionic surfactants.

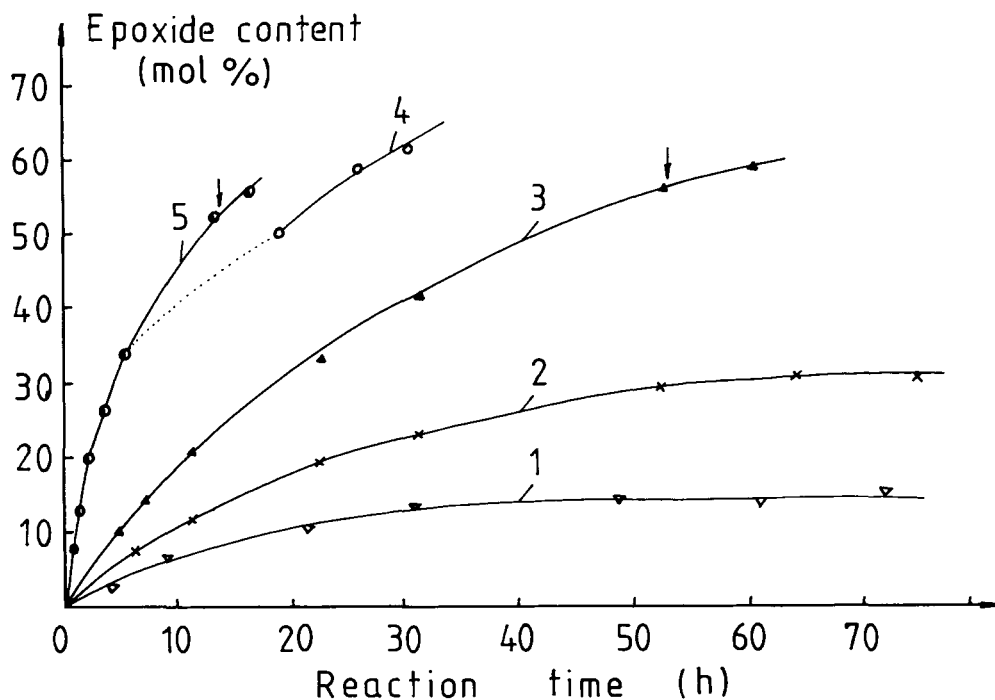


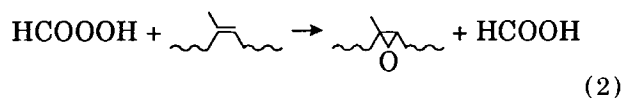
Figure 3 Variation of epoxide contents during *in situ* epoxidation process at 25 and 50°C. Conditions: (1) (∇) IP unit = 5.4 M/L; H_2O_2 /IP = 0.4 M/M; pH = 2.5; t_R = 25°C; (2) (\times) IP unit = 4.6 M/L; H_2O_2 /IP = 0.9 M/M; pH = 2.3; t_R = 25°C; (3) (\blacktriangle) IP unit = 2.3 M/L; H_2O_2 /IP = 2.8 M/M; pH = 2.2; t_R = 25°C; (4) (\circ) IP unit = 1.65 M/L; H_2O_2 /IP = 3.95 M/M; pH = 2.2; t_R = 50 and 25°C (dotted segment); (5) (\bullet) Conditions of epoxidation as in 4, t_R = 50°C.

Fig. 3, curves 1 and 2). The *in situ* epoxidation being fast enough, at 50°C it can lead to 50 mol % epoxide content after 10–12 h (see also Fig. 3, curve 5). The reaction could be performed both at high and low temperatures. Starting at 50°C, the epoxidation can also be continued at room temperature (evidently with lower rate; see an illustrative case in Fig. 3, curve 4) and vice versa. The reaction at room temperature is slower compared with that at 50°C and the epoxide content again is determined by the ratio between H_2O_2 and isoprene unit. The epoxidation could be accompanied by spontaneous coagulation at high epoxide contents, most frequently observed in latex system of higher dry rubber content (Fig. 3, curves 4 and 5, the moment of coagulation is indicated by a small arrow in the figure). So, in particular cases, the epoxidation tends to deteriorate the aggregative stability of latex, leading to coagulation. This fact reflects the profound changes in aggregative state of latex system submitted to chemical transformation. Macroscopically, the latex during epoxidation became more sticky due to the increasing epoxide content. The product obtained after coagulation in aqueous alcohol became softer

and it was easier to be pressed in thin sheet. In a special case, at higher epoxide content, latex spontaneously coagulated in fine particles as small, soft and porous pearl (of 0.1–1.5 mm diameter), ease to be filtered and washed. This phenomenon could be explained probably by gradual decreasing the protective capacity of nonionic and natural surfactant of latex during the epoxidation process. Actually, under the influence of mechanical, thermal, and chemical factors (stirring, collision, heating-cooling, and increasing the polarity of the epoxidized polymer), many perturbation factors can occur and develop, affecting both protection mechanisms (by electrical double layer and by sterical hindrance,¹⁷ leading finally to the spontaneous coagulation. Among these factors, the most important seemed to be the epoxidation itself. This process introduces profound changes in polarity and in structure of the original latex. Experiments made simultaneously with the same initial compositions, at 50°C and for 14 h, the first using continuous stirring and the second performed with only first 2 h of stirring showed that both proceed well, but the system without continuous stirring coagulated at an earlier stage of

epoxidation (the epoxide contents at the moment of coagulation were 57–58 mol % and 40–42 mol % for the first and the second case, respectively).

Schematically, the *in situ* epoxidation is performed by two consecutive reactions as follows:



We are inclined to support the hypothesis that the rate-determining step is the formation of the performic acid (reaction 1), as has been proposed earlier.⁷ This suggestion is now supported by several reasons. First, if the attack of performic acid on double bond is much slower than its formation, a clear accumulation of the peracid in system in very early stage of reaction should be observable and its concentration should be increased to a maximum, then gradually decreased. Simultaneously, net induction period should be visible. Actually, the concentration of performic acid determined during the epoxidation is very low (it ranges from 0.2 to 0.6 wt %) and reaction proceeds fast enough, without an induction period to relatively high epoxide content even at moderate temperature. These facts show that the attack of peracid on the double bonds is faster than its formation and the *in situ* epoxidation process will rapidly reach a stationary state (the rate of formation of performic acid is equal to its consumption).

Investigation on the Epoxidized Natural Rubber Products

The ENR products obtained from *in situ* epoxidation of NR present a large range of properties. Products of lower than 50 mol % epoxide content are typical elastomers, of opaque to translucent aspect, with off-white color. ENR of higher epoxide level becomes harder, reducing its elasticity. Structure of ENR was studied by infrared and ¹H-NMR spectroscopy, the glass transition temperature was measured by DSC technique. Products obtained after a long lasting reaction in acidic medium are accompanied by a small fraction of ring-opening derivatives proved by spectral and thermal analysis as has been shown for other similar cases.^{9,11}

Generally, using low concentration of formic acid and large excess of hydrogen peroxide, all the experiments were carried out without side ring-opening reactions and led to pure ENR products. In IR spectra, there are no presence of characteristic bands of

associated OH groups in the region of 3200–3600 cm⁻¹, of carbonyl ester groups at 1730–1740 cm⁻¹, and cyclic ether vibration at 1080–1100 cm⁻¹.^{9,10} Using the deformation band of methyl group (CH₃ at 1380 cm⁻¹) as internal standard, it is possible to follow the correlation between the double bonds (presented by *cis*-ethylene absorption band at 840 cm⁻¹) and the epoxide groups which appear and increase gradually during epoxidation. The results are presented in Figure 4, the absorbances of both groups were plotted against the real epoxide content of ENR determined by NMR and DSC techniques. It is seen that during the epoxidation, the concentration of the residual double bonds decreased continuously and it leveled up at approx. 62–65 mol %. The absorbance of epoxide groups correlates well with the epoxide content up to approx. 60–62 mol %; then a deviation from linearity appears (see Fig. 4).

In the ¹H-NMR spectra, typical peaks for hydroxyl or diol protons and cyclic ether at 3.4 and 3.9 ppm are not detectable. The NMR spectra show characteristic peaks for double bond and epoxide ring at 5.08 and 2.69 ppm, respectively. These peaks were used for quantitative analysis of epoxide content in ENR samples.¹³

The presence of new polar groups in the polymer backbone leads evidently to the change in the solubility of the material. This solubility of the ENR samples obtained from *in situ* epoxidation was studied in various solvents. Figure 5 shows gel (nonsoluble) fraction of a sample having moderate epoxide content (ENR-16, i.e., of 16 mol % epoxide group) in different solvents compared with the original NR. It is seen that the polar epoxide groups on the backbone affects clearly the solving capacity of the initial polyisoprene. The aliphatic nonpolar hydrocarbons (hexan, cyclohexan) and the very polar dimethyl formamide (DMF) are not good solvents for ENR-16. The ENR is more sensitive to moderate polar solvents. Thus, ethyl acetate, dioxane, tetrahydrofuran, and even more polar nitrobenzene are better solvents for ENR than for NR. The experiment showed that at a moderate modification level, epoxidation did not induce a great difference in behavior of ENR compared with the original NR toward good solvents for the last one (see Fig. 5, compare the gel contents in toluene, chloroform, tetrahydrofuran, and carbon tetrachloride for NR and ENR-16). The solubility of ENR products varies also with epoxide contents. Variation of gel content in toluene versus epoxide content for a set of samples is shown in Figure 6. It is seen that, tested in this weak polar solvent (dielectric constant $\epsilon = 2.4$ and dipole moment $\mu = 0.36$ Debye¹⁸), the products obtained at

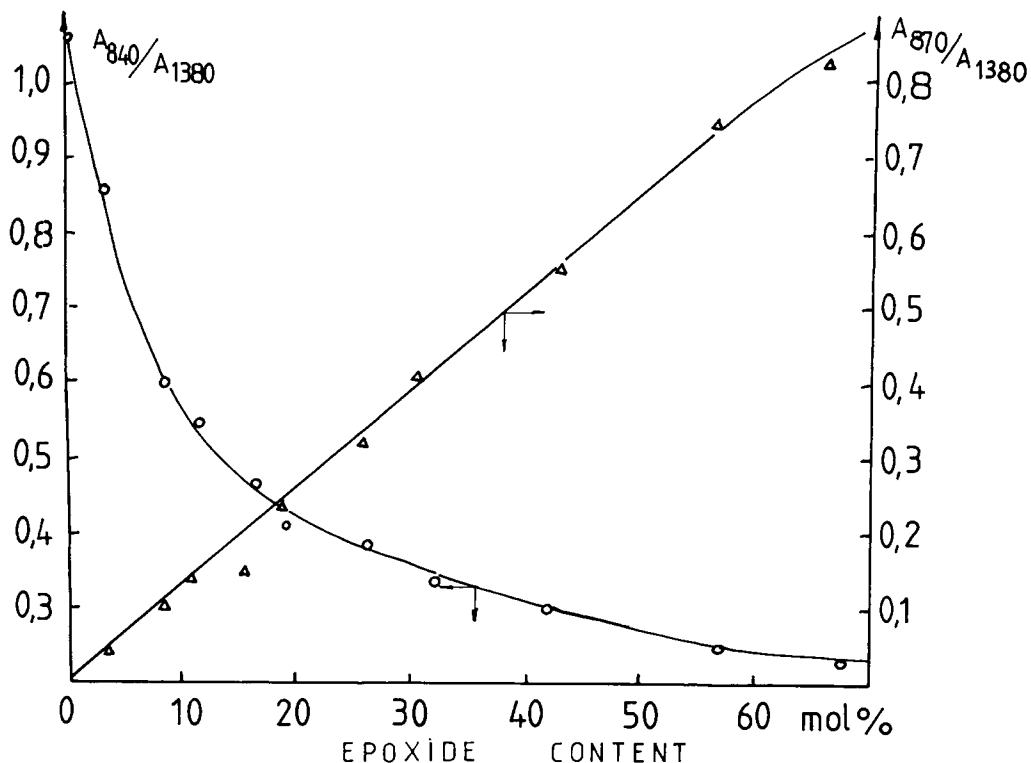


Figure 4 Correlation between the relative absorbances of *cis*-ethylene and epoxide IR band versus epoxide contents. Epoxide contents were determined by ¹H-NMR and DSC techniques.

longer reaction time and/or at higher epoxide content show an evident increase in gel content.

The sol fractions of ENR samples were studied for molecular weight and MWD by GPC technique,

using solution in THF. Results of this investigation are shown in Table III. It is seen that the epoxidation was accompanied by reducing molecular weight (of the soluble fraction) which depends on the reaction

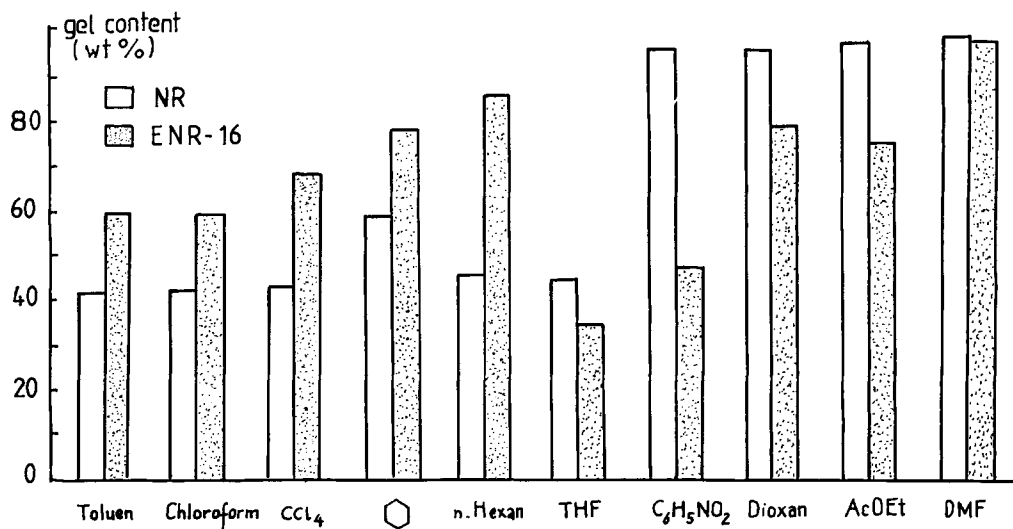


Figure 5 Gel contents of epoxidized natural rubber with 16 mol % epoxide group (ENR-16) in various solvents. Samples were synthesized at 25°C in 24 h, ratio H₂O₂/IP = 0.77 M/M, gel contents were determined at 25°C after 2 days of exposure.

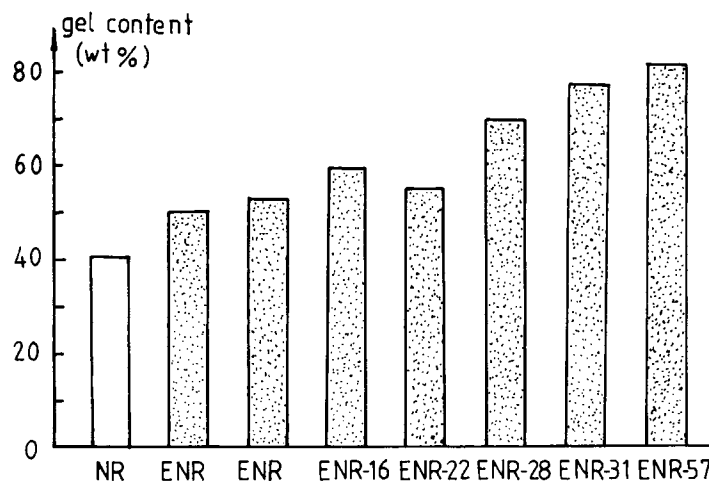


Figure 6 Variation of gel content versus epoxide content for a series of epoxidized natural rubber samples obtained by *in situ* reaction. Gel contents were determined in toluene at 25°C, 2 day exposure.

temperature. Higher reaction temperature reduced it more intensive than lower one (see Table III, compare lines 3 and 4). At moderate epoxide levels, the epoxidation process did not seriously affect molecular weight and MWD (see Table III, lines 1 and 2) but the epoxidized product shows a little more uniformity in MWD compared with the original NR (polydispersities were 2.65 and 3.43 for ENR-27 and NR, respectively). At high epoxide levels, the *in situ* epoxidation performed at lower temperature also proceeds better, leading to final product of much less gel content as compared with that at 50°C (see Table 3, lines 4 and 3).

CONCLUSIONS

Natural rubber latex having additional 3–5 phr nonionic surfactant of fatty alcohol ethyleneoxide condensate type (Verol S-15) is stable at pH 2 in the presence of formic acid. The stabilized latex can

be successfully subjected to subsequent *in situ* epoxidation.

This reaction can be performed with latexes of high dry rubber contents (effective concentration at room temperature is up to approx. 36% and at 50°C up to 28%), using a large range of H_2O_2 to isoprene unit (0.4–4.0 M/M) and large excess of H_2O_2 to $HCOOH$ (3–13 M/M).

The *in situ* epoxidized products are characterized by high purity (absence of side ring-opening derivatives). There is a close correlation between the IRS absorbances of the characteristic peaks for residual double bonds and epoxide groups versus the epoxide contents of the samples. The solubility and the gel content were studied in various solvents, demonstrating that epoxidation leads to increasing gel content at high epoxide levels and enhanced sensitivity of ENR to polar solvents. By GPC it was demonstrated for the sol fraction that the epoxidation process was accompanied by changes of MW and MWD of the original NR.

Table III Results of GPC Analysis for Epoxidized Natural Rubber Samples

Nr	Sample	t_R (°C)	Epoxide Content (mol %)	$M_n \times 10^5$	$M_w \times 10^5$	$M_z \times 10^5$	$M_v \times 10^5$	Disp.	Average MW	Gel ^a (wt %)
1	NR	—	0–1	1.72	5.92	15.23	5.92	3.43	5.14×10^5	34
2	ENR-27	50	27	1.53	4.05	7.74	4.05	2.65	4.79×10^5	40
3	ENR-57	50	50	0.45	1.67	5.61	1.67	3.72	1.23×10^5	76
4	ENR-58	25	58	1.01	3.42	8.33	3.40	3.38	2.74×10^5	55

^a Gel contents were determined in tetrahydrofuran at room temperature, 2 days exposed.

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