

Epoxidation of Natural Rubber in Latex in the Presence of a Reducing Agent

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SYNOPSIS

The *in situ* epoxidation of natural rubber latex was successfully performed in chain-scissoring conditions. The chain-scissoring process could be carried out simultaneously or successively to the epoxidation, to a determined extent. The rate and the degree of epoxidation depend on temperature, pH, and H₂O₂/isoprene units ratio. The chain-scissoring reaction leads to a limited intrinsic viscosity range and, at pH 2–3, it was practically completed in 24–40 h. The gel content of epoxidized natural rubber (ENR) products are markedly reduced in the presence of reducing agent. Infrared spectra of ENR, thus prepared, are characterized by the presence of a typical weak band at 1550 cm⁻¹, in addition to the other characteristic bands for normal ENR. At low pH and long-lasting reaction, the epoxide ring undergoes a ring-opening process, resulting in the formation of new OH, CO, ether groups, and slightly increased gel content. The Huggins constant, for a typical series of ENR obtained in redox conditions, was determined. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The study of the synthesis of epoxidized natural rubber (ENR) in latex by different methods, and investigation of the structure and properties of this material, are of interest.^{1–5} The epoxidation of natural rubber (NR) is one of the most important and promising ways to obtain new polymeric material from a renewable resource, due to the high performances and good properties of ENR. This reaction of NR in latex can be successfully performed with preformed peroxy acids^{1,2} or by the *in situ* method,^{3,5,8–10} leading to a large range of ENR products. On the other hand, the degradation of the NR chain, under the influence of a redox system, was demonstrated by Brosse et al.⁷ for the phenylhydrazine/O₂ couple. The intensity and the extent of the chain scissoring reaction depend upon temperature, reaction time, and concentration of the reducing agent. By degradation of NR into shorter chain segments, it was possible to obtain liquid natural rubber (LNR) with useful and interesting technological

applications. The LNR is also an intermediate for further chemical transformations, for example, in synthesis of a thermoplastic block copolymer (with synthetic monomers).⁶ The possibility of epoxidation of LNR was pointed out previously by using perphthalic acid⁷ or recently by *in situ* methods.^{8–10}

Despite the abovementioned works, there has not been a detailed study on the influence of the chain-scissoring reaction on the epoxidation process and on the structure of the final product. This article presents results of the epoxidation of NR in latex in the presence of a reducing agent, and investigates the correlation between reaction conditions and properties and the structure of the ENR, obtained under such a treatment.

EXPERIMENTAL

Materials

Natural rubber latex used was centrifuged, full ammonia latex of 58% dry rubber content (drc) (Alcantex, Alcan Safric Co.). The surfactant used was fatty alcohol ethylene oxide condensate, nonionic class Verol S-15 (Verila, Bulgaria), with a cloud point of 72–75°C. The hydrogen peroxide (purum)

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used was 30% aqueous solution (Fluka). Also used were sodium nitrite (purum, Merck), formic acid (p.a.) of 98% (Ferak), and tetrahydrofuran (HPLC purum, Merck).

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

Procedure

Chain-Scission Parallel with Epoxidation

NR latex, 58% drc, was stabilized by 3–5 parts per hundred of rubber (phr) of 15–20% aqueous solution of Verol S-15. This latex, under continuous stirring, was acidified by HCOOH to the necessary pH, then was treated successively with 30% aqueous H₂O₂ (ratio of H₂O₂ to isoprene units was 0, 6–0, 9 M/M) and a 20% solution of NaNO₂. The reducing solution must be added slowly to avoid the excessive development of heat and nitrogen oxides. The ratio of NaNO₂ to dry rubber was 1–5 phr. The reaction could be performed at room temperature (23–25°C) or at thermostated regime (40–50°C) for a determined time. At various time intervals, samples were taken, were coagulated, and were then subjected to analysis for epoxide content, gel-sol content, spectral analysis, or to viscosity determination. At the end of process, pH was increased to *ca.* 8–8.5 by using 25% NH₄OH in order for the reaction to be terminated; the rest of the H₂O₂ was to be destroyed. The product was then coagulated in ethanol, was filtered, was washed with distilled water, was pressed into a thin sheet, and was dried to constant weight under vacuum at 40°C.

Chain-Scission After Epoxidation

In-situ epoxidation proceeded as usual.⁹ After reaching a necessary epoxide level, a solution of NaNO₂ was introduced and the whole system was allowed to react for an additional 48–192 h. The rest of method was similar to the preceding one that was described in *Chain-Scission Parallel with Epoxidation*.

Analysis

Epoxide Content

Low levels of epoxide content (lower than 15 mol %) were determined by direct chemical titration with HBr in glacial acetic acid in the presence of crystal violet as an indicator (method of Durbetaki¹¹). Higher epoxide contents were determined by instrumental methods via IR analysis (method of

Davey and Loadman¹²), ¹H-NMR analysis,¹³ or by DSC analysis (via determination of glass transition temperature, *T_g*).¹³

Accuracy of the analytical tests utilized in the corresponding range of epoxide content was within 1–1.5 mol %. Comparative data of epoxide content, determined by different methods, were presented previously.⁴

Gel content (nonsoluble fraction) was determined in tetrahydrofuran (THF) at room temperature, using a standard method.¹⁴

Viscosity of the polymer was determined in diluted THF solution, using an Ubbelohde viscometer.

Apparatus

IR spectra were recorded on a Specord M-80 spectrometer (Carl-Zeiss, Jena), using film cast on KBr windows. ¹H-NMR spectra were recorded on a Jeol-JNM-100, from CDCl₃ solutions.

T_g values of ENR samples were determined as onset values by the thermal analysis data station and a DSC-2C apparatus (Perkin-Elmer).

Viscometry was performed with an Ubbelohde viscometer, using an ultrathermostate (Schott, model CT-1150).

RESULTS AND DISCUSSION

In the presence of *in situ* prepared performic acid and a reducing agent (NaNO₂), two parallel reactions occur: in addition to the epoxidation, a chain-scissoring process also proceeds, due to the existing redox conditions (NaNO₂/H₂O₂ system). When the reducing agent was introduced simultaneously with H₂O₂, the chain-scissoring reaction can be performed together with epoxidation. As seen in Figure 1, even in the presence of a reducing agent and a competitive chain-scissoring process, the epoxidation proceeded well. At moderate temperature (25°C), epoxidation led to relatively high epoxide levels, up to 40–50 mol % epoxide groups (Fig. 1, curve 1). In the presence of *ca.* 3, 5 phr NaNO₂ and at low pH, the chain-scissoring reaction proceeded rapidly in the first 10 h and it was practically completed in 24 h. The intrinsic viscosity of samples reduced quickly in the first 10 h from 4.1 dL/g to 1.08 dL/g, then leveled off at *ca.* 0.8 dL/g (Fig. 1, curve 2). During this time, the gel content quickly reduced from *ca.* 40% to 2–3%, but at long-lasting reaction, the gel content began to increase slowly again, probably due to some side reactions of ENR leading to partial crosslinking.

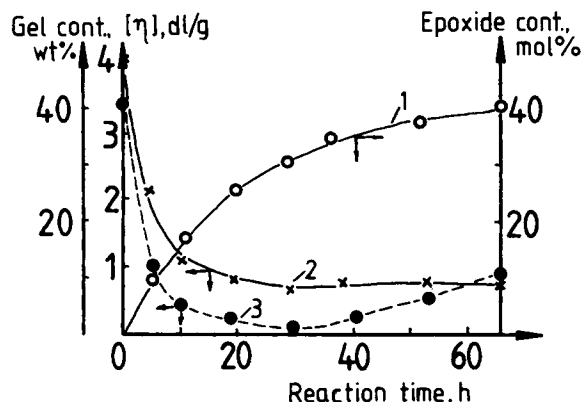


Figure 1 Epoxidation of natural rubber latex in the presence of reducing agent (NaNO_2). $\text{H}_2\text{O}_2/\text{isoprene} = 0.77 \text{ M/M}$, $\text{NaNO}_2 = 3.4 \text{ phr}$, $\text{pH} = 2.2$, $t = 25^\circ\text{C}$. (O) epoxide content, mol %; (X) intrinsic viscosity, dL/g; (●) gel content, wt %.

The chain-scission could be applied also to epoxidized NR latex, leading to reduction both of the gel content and the molecular weight (mol wt) of ENR product. Figure 2 presents the results of a study on a system for which the reducing agent was introduced into NR latex, which had preliminarily been epoxidized for 24 h at 45°C . It is seen that, in the initial period (0–24 h), up to the addition of the reducing agent, the epoxidation proceeded normally, resulting in increasing epoxide content, while the intrinsic viscosity and the gel content slowly decreased. By introducing NaNO_2 (the moment of introduction was indicated by a small arrow on the

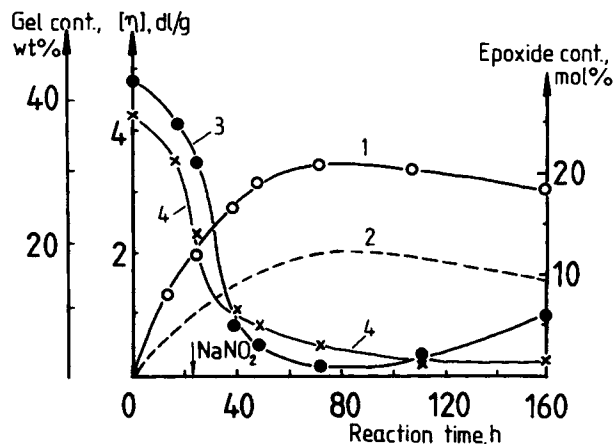


Figure 2 Chain-scission in preliminary epoxidized natural rubber latex. $\text{H}_2\text{O}_2/\text{isoprene} = 0.89 \text{ M/M}$, $\text{NaNO}_2 = 3.5 \text{ phr}$, $\text{pH} = 3$, $t = 45^\circ\text{C}$. (O) epoxide content, mol %; (---) epoxide content, mol %, for the same system but $\text{pH} = 6$; (●) gel-content, wt %; (X) intrinsic viscosity, dL/g.

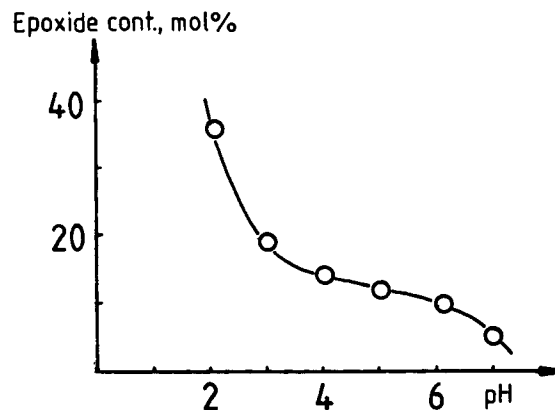


Figure 3 Variation of epoxide content vs. pH. $\text{H}_2\text{O}_2/\text{isoprene} = 0.85\text{--}0.90 \text{ M/M}$; $\text{NaNO}_2 = 3.2\text{--}3.5 \text{ phr}$; reaction time = 162 h.

axis of the abscissa in Fig. 2), the chain-scission became the prevailing process, leading to a rapid decrease in both the gel content and the intrinsic viscosity of products (see Fig. 2, curves 3 and 4, respectively). At the same time, the epoxidation continued to proceed and the epoxide content increased to a maximal value in ca. 70 h. At 45°C , in acidic medium ($\text{pH} 3.0$) and long-lasting process ($> 70 \text{ h}$), the epoxidation was accompanied by side ring-opening reactions, slowly reducing the epoxide con-

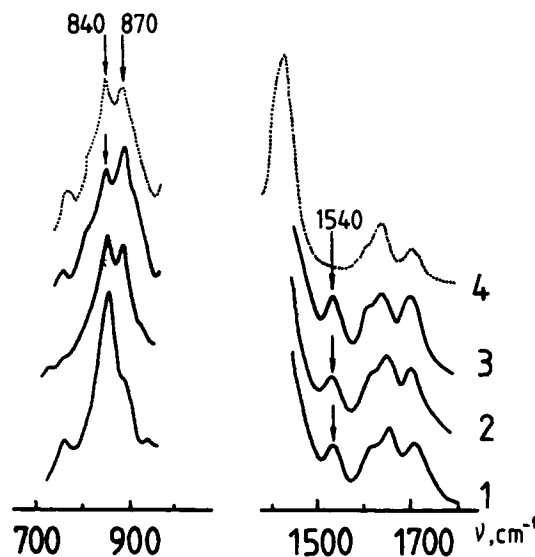


Figure 4 Variation of characteristic IR spectral bands for ENR samples prepared by *in situ* epoxidation in the presence of reducing agent. (1) ENR-11, (2) ENR-29, (3) ENR-40, (4) (---) ENR-30, prepared without reducing agent. Number following ENR indicates the epoxide content in mol %.

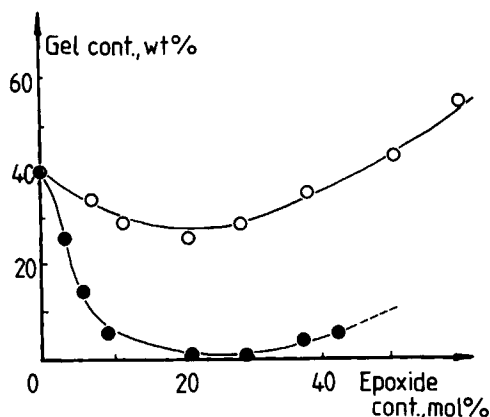


Figure 5 Variation of gel content vs. epoxide content. (○) normal epoxidation by *in situ* prepared performic acid at 50°C; (●) epoxidation in presence of 3.4 phr NaNO₂ at 25°C.

tent and increasing the gel content of the final products (Fig. 2, curves 1 and 4, respectively).

The rate and the extent of epoxidation depend also upon the reaction pH. The lower the pH, the higher the reaction rate and the higher the final epoxide content, as presented in Figure 2 (compare curves 1 and 2 for reaction at pH 3 and 6, respectively).

Experiments at various pH, for systems of the same H₂O₂/isoprene ratio and NaNO₂ content, showed that the *in situ* epoxidation in redox conditions was highly favorable at low pH (pH 2.2–3) (Fig. 3), whereas at pH 6–7 epoxidation proceeded with a low rate and led to a low epoxide content. This is probably due to the low rate of formation of performic acid and to the increased rate of decomposition of H₂O₂ at higher pH.

Depending on the degree of chain-scission, the ENR obtained can be light yellow to yellow in color, having from typically elastomeric aspect to sticky, soft material with self-creeping properties, just as liquid NR, and can be used as LNR or as pressure-sensitive adhesive (directly as latex or as solution in a suitable solvent).

The structure of ENR, obtained under redox condition, was studied in detail by IR spectroscopy. Figure 4 shows typical IR spectra for a series of ENR samples prepared in redox conditions. These products differed from normal *in situ* epoxidized NR by the presence of a new characteristic weak to medium band for unsaturated aliphatic nitro group at the 1530–1550 cm⁻¹ region.¹⁶ The ENR products, obtained after a long-lasting reaction in high acidic medium, can show the presence of additional bands that are characteristic for ring-opening products (ether, alcohol, carbonyl, formate⁴), the most outstanding among them being the OH band in the 3200–3580 cm⁻¹ region. The chain-scissoring reaction led to a lowering of the molecular weight and to products of high content of OH groups. Compared with normal *in-situ* epoxidation, the reaction in the presence of a reducing agent results in products of much lower gel content, as shown in Figure 5.

On the other hand, the epoxidation leads also to profound changes in the original structure of the NR. The reduced mol wt and the structural changes should lead to a change in the interactions between polymer and solvent, which, in its turn, should reflect in the value of the Huggins' constant, k' , in the corresponding, well-known equation.¹⁵

The results of the calculation of Huggins' constant for a series of ENR products, obtained in redox conditions, is shown in Table I.

It is seen that Huggins' constant falls in the range of normal values only at low modification level, when mol wt has not changed substantially. The constant reveals abnormally great values for samples of higher epoxide content and low mol wt, suggesting the difference in the intensity or nature of interactions between the modified polymer and solvent in these cases.

CONCLUSIONS

The *in situ* epoxidation can be performed successfully in chain-scissoring conditions. The rate and

Table I Molecular Parameters for ENR Samples Obtained by *in Situ* Epoxidation in Presence of NaNO₂^a

React. Time (h)	0	15	24	40	48	114	162
Epox. Content (mol %)	1	6	9.5	21	19	18	17.2
[η] (dL/g)	4.15	3.13	2.18	0.39	0.315	0.30	0.28
k'	0.838	0.381	0.429	2.83	3.52	4.27	4.73

^a Reaction conditions as in Figure 2.

the extent of epoxidation depend on temperature, pH, and H₂O₂/isoprene ratio. The chain-scission could be carried out simultaneously or successively to the epoxidation, resulting in reduced gel content and mol wt of ENR. At pH 2.2–3.0 this process is practically complete in 24 h at moderate temperature. Beside the characteristic bands for normal ENR, the IR spectra of ENR, thus prepared, reveal a typical weak band at 1540–1550 cm⁻¹. At low pH and long-lasting conditions, the ring-opening reactions occur, resulting in new side groups and slightly increased gel content. The Huggins constant was determined for a series of ENR; abnormal great values for samples of higher epoxide content and low mol wt were found.

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Received September 17, 1992

Accepted December 14, 1992