

## Epoxidation of low-molecular-weight *Euphorbia lactiflua* natural rubber with “in situ” formed performic acid

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### SUMMARY

The epoxidation of low-molecular-weight natural rubber isolated from *Euphorbia lactiflua* latex was accomplished. The reaction was performed using formic peracid formed “in situ” from hydrogen peroxide and formic acid. Different temperatures, ratio of H<sub>2</sub>O<sub>2</sub> to isoprene units and H<sub>2</sub>O<sub>2</sub> to HCOOH were used. The products were characterized by infrared spectroscopy (IR), <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC) and elementary analysis. <sup>1</sup>H-NMR was used quantitatively to calculate epoxidation levels. Maximum epoxidation reached was 89.4%. DSC results record a linear relationship between percent epoxidation and T<sub>g</sub>.

### INTRODUCTION

*Euphorbia lactiflua*, a shrub that grows in arid regions in Chile, has been selected as a potential renewable source of natural rubber (NR), *cis*-1,4 polyisoprene (1-2). This polymer has a low molecular weight, 8.4 x 10<sup>4</sup>, compared with the NR of the rubber tree (*Hevea brasiliensis*) or guayule *Parthenium argentatum*, 1.3 x 10<sup>6</sup> (3), and it is unsuitable for high-performance applications. Therefore the utilization of this low molecular weight rubber (LMWER) is important in establishing *E. lactiflua* as a source of natural rubber and will require taking advantage of the particular physical and chemical properties of LMWER. This polymer could find direct use as a plasticizer or processing aid because of its low viscosity (4,5). Alternatively, LMWER could serve as a feedstock for production of high value, speciality polymer derivatives analogous to those produced from NR.

NR has been used as feedstocks for chemical modifications, including epoxidation (6-10) chlorination and maleination (11,12), to produce functionalized speciality polymers with an expanded range of physical and chemical properties.

Among many possibilities of chemical modifications of NR, epoxidation is a simple and efficient method to introduce a new reactive group into the polyisoprene backbone, leading to new and useful properties (5,8). Several publications and patents have appeared in this field in the past few years (5-10).

It was found that, from an economic point of view, the “in situ” formed performic acid process seems to be more desirable due to the easy availability and low cost of the reagents. The main problems associated with the “in situ”

formed performic acid route is the formation of various secondary ring-opened and ring-expanded products, viz., hydroxyls, esters (formate), hydrofuran, etc. (6).

The objective of the present investigation is to study different parameters such as reaction time, temperature,  $\text{H}_2\text{O}_2$  and  $\text{HCOOH}$  concentration to develop optimum process conditions for the highest yield of epoxy groups with the least possible amount of secondary reaction product formation. In this paper, the formation and characterization of LMWER in various epoxidation levels is reported. Percent epoxidation has been determined using NMR; DSC has been used to support findings.

## EXPERIMENTAL

### Materials

Natural rubber (LMWER): Fresh latex from *E. lactiflua* was mixed with  $\text{C}_2\text{Cl}_4$ . After removing the azeotrope, the solid was dried at  $50^\circ\text{C}$  for 12 hours. Dry latex was dissolved in  $\text{CH}_2\text{Cl}_2$ , then filtered, and the solution was added drop by drop to methanol. The precipitate was centrifuged, dried at  $50^\circ\text{C}$  for 12 hours, then in a vacuum dryer at room temperature for 2 hours and weighed. The yield was from 14.6 to 20.8% on dry weight basis. The characterization was done by FT-IR, NMR spectroscopy ( $^{13}\text{C}$  and  $^1\text{H}$ ), GPC and DSC. Formic acid (98-100%) pa ACS Merck; hydrogen peroxide (30%) pa Merck; sodium lauryl sulfate (95%) Sigma.

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

### Epoxidation

A two neck 100 ml round bottomed flask fitted with a condenser and separatory funnel was charged with a molar amount of LMWER dissolved in benzene (7.5 w/w solution), the desired molar amount of 98% formic acid (Table 1) and  $1.9 \times 10^{-4}$  g/ml of benzene of surfactant (lauryl sulfate). The mixture was placed on a magnetic stirring device and the funnel was charged with the desired molar amount of 30% hydrogen peroxide (Table 1). The mixture was heated and stirred at  $30^\circ$  or  $65^\circ\text{C}$  for 15 min, at which point the hydrogen peroxide was added drop by drop over a 15-20 min period. The final mixture was maintained at  $30^\circ$  or  $65^\circ\text{C}$  from 6 to 30 hours (Table 1). After epoxidation, sufficient aqueous sodium carbonate was added to neutralize the acid, and the final aqueous layer removed by decantation. The organic phase was then poured into methanol to coagulate the epoxidized rubber. This crude product was dissolved in  $\text{CH}_2\text{Cl}_2$ , added to methanol for coagulation, centrifuged and vacuum dried to constant weight before analysis.

### Analysis

The molecular weight of *cis*-1,4-polyisoprene from *Euphorbia lactiflua* was determined by gel permeation chromatography (GPC). Analyses were run in tetrahydrofuran (THF) solution (0.5% w/v) at room temperature on a Bruker L 21B

GPC apparatus equipped with Bruker 4000-40000; 40000-400000, 1000 Å columns and refractive universal index detector using a polystyrene calibration.

Infrared analyses were performed on a Nicolet System Magna-IR 550 spectrometer, using films cast on NaCl windows.

$^{13}\text{C}$  and  $^1\text{H}$ -NMR spectra were obtained on a Bruker AC 250P 250 MHz nuclear magnetic resonance spectrometer using deuterated chloroform as solvent with tetramethylsilane as internal reference. ELMWER epoxide contents were determined by  $^1\text{H}$ -NMR. The relative areas of the peaks assigned to hydrogen bonded to oxirane carbon ( $\delta = 2.9$  ppm) and hydrogen bonded to olefinic carbon ( $\delta = 5.1$  ppm) were compared (5-10).

Polymer glass transition temperature ( $T_g$ ) were determined by differential scanning calorimetry at  $10^\circ\text{C min}^{-1}$  under a nitrogen atmosphere from  $-90$  to  $100^\circ\text{C}$  on a DSC V4.08 Du Pont 2100 Model V.4.

## RESULTS AND DISCUSSION

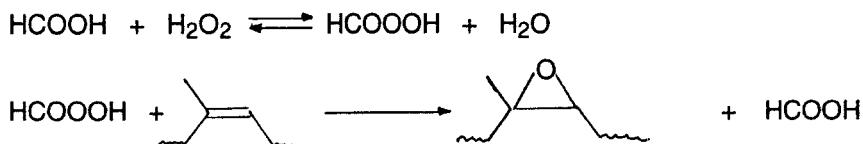
### *Isolation and characterization of E. lactiflua rubber*

LMWER was isolated from *E. lactiflua* latex following the fractionation method given in the Experimental section. The yield from different samples were from 12.6 to 20.8% on dry weight basis. FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra agreed with those given in literature (5-9) for *cis*-1,4-polyisoprene.

GPC analysis gave  $M_w = 83570$  and  $M_n = 48300$ , with a MWD ( $M_w/M_n$ ) of 1.7. The intrinsic viscosity of LMWER was  $0.58 \text{ dl g}^{-1}$  and it is suitable for industrial purposes.

### *Epoxidation*

Although a variety of peracids may be used to perform the epoxidation (6,7,10,13), "in situ" formed performic acid was chosen due to its availability, reactivity and economy (6). Schematically, "in situ" epoxidation is performed by two consecutive reactions as follows:



The first step, formation of peracid by the action of  $\text{H}_2\text{O}_2$  with the acid, is a slow and endothermic reaction, and the second step, the epoxidation, is fast and exothermic (7,11). Previous work has shown that the epoxidation of unsaturated bonds in a polydiene with organic peracids does not cause main chain fission (14). The extent of epoxidation and the formation of various secondary ring opened and ring expanded products viz., hydroxyl, esters, hydrofuran, etc. depends mainly on the ratio  $\text{H}_2\text{O}_2$  to isoprene unit, ratio  $\text{H}_2\text{O}_2$  to  $\text{HCOOH}$ ,

temperature and reaction time. The mechanism of the formation of these side products was explained by Gelling (15) and Perera et al. (15).

The conditions used and the results obtained in this work are given in Table 1. The reactions were carried out in polymer solutions (7.5% w/w) in benzene.

Table 1. LMWER reaction conditions, epoxidized low molecular weight *E. lactiflua* rubber (ELMWER) epoxide content and glass transition temperature (T<sub>g</sub>).

Run N <sup>o</sup>	Reaction conditions		Reactant mol ratios <sup>a</sup>		ELMWER	
	Time (1 h)	T (°C)	H <sub>2</sub> O <sub>2</sub> /C=C	H <sub>2</sub> O <sub>2</sub> /HCOOH	Epoxide content <sup>b</sup> (%)	T <sub>g</sub> <sup>c</sup> (°C)
1	8	65	0.5	3.3	-	-
2	24	65	0.5	3.3	-	-
3	8	30	1	1	63.9	-9.74
4	24	30	1	1	85.6	13.32
5	6	30	1.5	3	66.9	-8.32
6	20	30	1.5	3	89.4	16.36
7	30	30	1.5	3	73.3	18.45

a) Mol ratio of hydrogen peroxide to carbon-carbon double bonds in LMWER and mol ratio of hydrogen peroxide for formic acid.

b) Calculated via <sup>1</sup>H-NMR

c) Obtained from DSC analysis, T<sub>g</sub> = -65.9°C for LMWER

### **Effect of temperature and reaction time**

It was found (Table 1), that the extent of epoxidation strongly depends on the temperature. In the runs carried at 65°C the polymer came out of benzene solution after about 3 hours. The resulting products were intractable masses with high gel contents typical of crosslinked polymer. An increase in the secondary reaction products with an increase in the epoxidation temperature has been reported (5,6). These products could arise by side reactions due to hydroxylic radicals and to free oxygen that produces peroxide radicals in the chain. Also secondary reaction products may arise from opening of oxirane rings, forming cycles, diols, ethers and furane groups (15).

At 30°C maximum conversions of available peroxide were obtained after 20-24 h. For example, runs 3 and 4 or 5 to 7 listed in Table 1 represent an identical sample mixture maintained for different times. The epoxidation increases as the time increases. Nevertheless, after a certain time, (approx. 20 h) the percent of epoxidation decreases mainly due to the secondary reactions with the formation of furane, hydroxyl and formate groups (5, 6, 16). <sup>1</sup>H-NMR spectra of ELMWER after 20 and 30 hours of reaction (runs 6 and 7) are shown in Figure 1. The resonance at  $\delta=3.3$ , C, ppm attributed to H adjacent to a hydroxyl group, in the ELMWER obtained after 30 h of reaction, confirms the formation of secondary products.

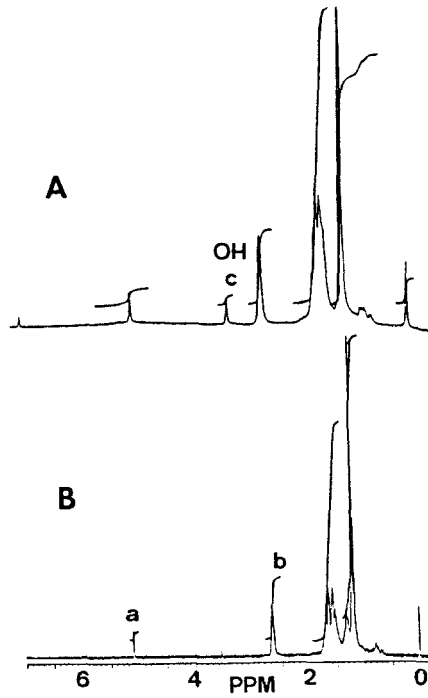


Figure 1.  $^1\text{H}$ -NMR spectra of ELMWER with relevant assignments. **A.** 20 h of reaction (89,4% epoxidation). **B.** 30 h of reaction (73,3% epoxidation). Both  $\text{H}_2\text{O}_2/\text{C}=\text{C} = 1.5$  and  $\text{H}_2\text{O}_2/\text{HCO}_2\text{H} = 3.0$ .

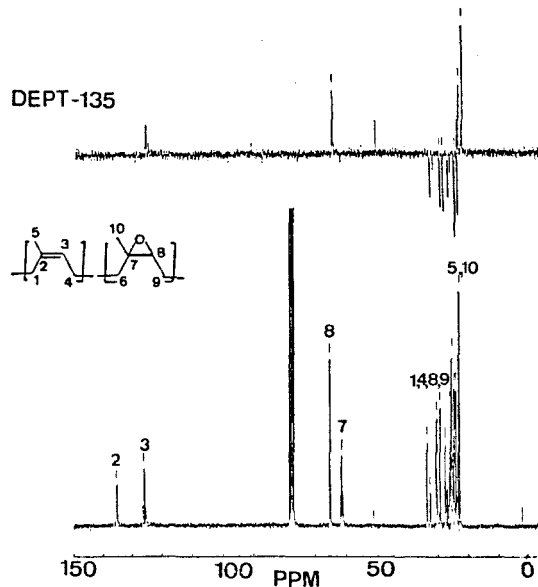


Figure 2.  $^{13}\text{C}$ -NMR spectrum of ELMWER (66,9% epoxidation) and DEPT at  $135^\circ$  with relevant assignments.

$^{13}\text{C}$ -NMR studies established that for all the degrees of epoxidation obtained in this work, the process is quite random, in agreement with the results obtained previously in the epoxidation of *Hevea* and guayule natural rubber (9, 13, 14). The  $^{13}\text{C}$ -NMR spectrum of 66.9% epoxidized LMWER is shown in Figure 2, along with the DEPT at  $135^\circ$ . Assignments were made on the basis of  $^{13}\text{C}$ -NMR studies reported by Bradbury and Perera (14) and DEPT experiments at  $90^\circ$  and  $135^\circ$ .

### ***Effect of $\text{H}_2\text{O}_2$ and $\text{HCOOH}$ concentration***

The results in Table 1 show that an excess of  $\text{H}_2\text{O}_2$  (molar ratio  $\text{H}_2\text{O}_2/\text{C}=\text{C} = 1.5$ ), allows to obtain higher percents of epoxidation in the final product at an early stage of the reaction (runs 5 and 6 vs runs 3 and 4).

On the other hand, it was found that a higher ratio of  $\text{H}_2\text{O}_2/\text{HCOOH}$  leads to a higher epoxidation level in the final product. This observation may be explained by the phenomena of ring opening of epoxy groups and hydrofuranization, both of which were found to be accelerated in the presence of acid medium (16,17). In the product obtained in run 4 ( $\text{H}_2\text{O}_2/\text{HCOOH} = 1.0$ ) after 24 h of reaction, in both FT-IR and  $^1\text{H}$ -NMR spectra the presence of characteristics bands of OH groups in the region of  $3200\text{-}3600\text{ cm}^{-1}$  and at  $\delta = 3.4$  ppm, respectively, were found. On the other hand, these signals were detected in run 7 ( $\text{H}_2\text{O}_2/\text{HCOOH}=3$ ) only after 30 h of reaction.

### ***Effect of the epoxidation on the glass transition temperature***

The glass transition temperature ( $T_g$ ) of LMWER and ELMWER of various epoxidation levels was determined by DSC analysis. ELMWER samples show a direct relationship between the epoxide content and  $T_g$ : for every percent increase in epoxide content, a  $T_g$  increase of  $0.6$  to  $1.0^\circ\text{C}$  have been reported (5, 12). Our findings (Table 1) are consistent with these results, giving an average of  $0.9^\circ\text{C}$  of  $T_g$  increase for every percent increase in epoxide content, except for the product in run 7 (increase of  $1.15^\circ\text{C}$  in  $T_g$  for percent increase in epoxide content) where side ring-opening reaction was observed. Thus, DSC can be used as a quantitative measure for the extent of epoxidation when secondary reactions are absent.  $T_g$  is related to polymer modulus, the ability to respond to applied stresses. A higher- $T_g$  polymer will have a higher modulus. Specifying the epoxide content of ELMWER could be used to control the stress-strain characteristics of the composition (5).

## **CONCLUSIONS**

The formation and characterization of ELMWER has been performed through reaction of olefinic bonds with "in situ" formed performic acid. The structure of epoxidized rubber has been confirmed by NMR, FT-IR and DSC. Quantification of the extent of epoxidation can be determined by DSC and NMR spectroscopy. The maximum epoxidation 89.4% was achieved at  $30^\circ\text{C}$  with  $\text{H}_2\text{O}_2/\text{C}=\text{C} = 1.5$  and  $\text{H}_2\text{O}_2/\text{HCOOH} = 3$ , after 20 h of reaction. The effect of epoxidation on  $T_g$  follows a linear relationship with mol % epoxidation. ELMWER is soluble in organic solvents and can be utilized as an additive for coating that imparts flexibility to otherwise rigid epoxy systems.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. Gnecco, S., Bartulín, J., Marticorena, C., Ramírez, A. *Biomass*, **15**, 165 (1988).
2. Gnecco, S., Cid, R., Caamaño, V., Pavlath, A.E. *ACS Div. Fuel Chem.*, **36**(2), 702 (1991).
3. Swanson, C.L., Buchanan, R.A., Otey, F.H. *J. App. Polym. Sci.*, **23**, 743 (1979).
4. Marteau, J., Croissandeau, M.C. *Compte Rendu Conf. Int. sur le Caoutchoc Naturel Liquide*, Abdijan (1986) pp. 42-62.
5. Schloman Jr., W.W. *Ind. Crops & Prod.*, **1**, 35 (1992).
6. Sanjoy, J., Gupta, B.R., Maiti, B.R. *Ind. Eng. Chem. Res.*, **30**, 2573 (1991).
7. Viet Bac, N., Terlemezyan, L., Mihailov, M. *J. App. Polym. Sci.*, **42**, 2965 (1991).
8. Viet Bac, N., Terlemezyan, L., Mihailov, M. *J. App. Polym. Sci.*, **50**, 845 (1993).
9. Vernekar, S.P., Sabne, M.B., Patil, D., Patil, A.S. et al. *J. App. Polym. Sci.*, **44**, 2107 (1992).
10. Viet Bac, N., Mihailov, M., Termelezyan, L. *Eur. Polym. J.*, **27**(6), 557 (1991).
11. Bocaccio, G., de Livoniere, H. *L'Actual. Chim.*, **2**, 100 (1991).
12. Bocaccio, G. *Compte Rendu Conf. Int. sur le Caoutchoc Naturel Liquide*, Abdijan (1986) pp. 132-148.
13. Thames, S.F., Poole, P.W. *J. App. Polym. Sci.*, **47**, 1255 (1993).
14. Bradbury, J.H., Perera, M.C.S. *J. App. Polym. Sci.*, **30**, 3365 (1985).
15. Gelling, I.R. *Rubber Chem. Technol.*, **58**, 86 (1985).
16. Perera, M.C.S., Elix, J.A., Bradbury, J.H. *J. Polym. Sci. Part A*, **26**, 637 (1988).
17. Burfield, D.R., Lim, K.L., Law, K.S. *J. App. Polym. Sci.*, **29**, 1661 (1984).