

Chemical Modification of Polydienes in Latex Medium: Study of Epoxidation and Ring Opening of Oxiranes

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ABSTRACT: Referring to previous work carried out in organic solvents, a study of the action of nucleophilic reagents on epoxidized units of 1,4-epoxidized polyisoprene (synthetic polyisoprene or natural rubber) was performed in latex medium. Among the considered reagents, dialkylphosphate and ammonium diethyldithiophosphate demonstrated the ability to add under these reaction conditions on epoxidized units according to a SN2 substitution with an oxirane ring-opening mechanism. A systematic study was performed with dibutylphosphate that was shown to be

very reactive. Grafting of phosphorated groups along polyisoprene chains was carried out via reaction of the acidic function (P-OH) of the phosphate with oxirane rings previously created on a 1,4-polyisoprene backbone. The prominent role of latex pH on the reaction was shown. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 39–52, 2005

Key words: rubber; modification; functionalization of polymers; epoxidation; latex; dibutylphosphate

INTRODUCTION

Chemical modification of synthetic and natural rubbers has been, for many years, a convenient method of producing new polymers.^{1,2} Most of these works were performed in bulk or in organic solvent. The purpose of this paper is to perform chemical modifications without solvent, by carrying out the chemical reactions in latex medium, allowing for great process simplification. A well-known example of successful chemical modification of natural rubber performed in latex medium is epoxidation.^{3,4} This modification is important due to the great reactivity of oxirane rings toward nucleophilic reagents. For example, reactions with amine,⁵ carboxylic acid,^{6,7} alcohol,^{8,9} and phosphoric acid derivatives,^{10,11} have been studied on epoxidized polyisoprene in solution.

The purpose of the present paper is to relate some rubber chemical modification results obtained in latex medium. Reaction of nucleophiles with epoxidized natural rubber (NR) latexes was considered. As the composition of NR latex is extremely complex, chemical modifications performed on natural rubber latexes were compared with those carried out in same conditions using a synthetic 1,4-polyisoprene latex (LIR-700 latex from Kuraray Company). In a first stage, the epoxidation of the two latexes was studied, and the

results obtained by considering simultaneously the parameters able to influence the epoxidation rates were compared.¹² The ring opening by nucleophilic reagents, especially dibutylphosphate (DBP), was then considered.

EXPERIMENTAL

Materials

Natural rubber latex was a centrifuged latex of 60% dry rubber content (DRC), stabilized with ammonia to avoid the rubber coagulation. It was composed of *cis*-1,4-polyisoprene (head–tail sequences), plus non-rubber compounds (water, lipids, proteins, carbohydrates, minerals, etc). Particle diameter in the latex was between 0.01 and 5 μm , and the rubber average molecular weight was $0.25 \times 10^6 < \overline{M}_n < 2.7 \times 10^6$ (presence of a gel fraction). Synthetic polyisoprene latex (LIR-700) was supplied by Siber Hegner Company (Kuraray product). It was prepared by emulsification of a synthetic polyisoprene ($\overline{M}_n = 29,000$) having the following microstructure: 66% *cis*-1,4-, 27% *trans* 1,4-, and 7% 3,4-. The particle diameter in the latex was about 0.35 μm .

Dichloromethane (technical grade) was dried on calcium sulphate, filtered, and then distilled on phosphoric anhydride after 1 h reflux. Methanol (technical grade) was distilled on calcium sulphate and then stored on 3 Å molecular sieves. Formic acid and 35% hydrogen peroxide were purchased from Acros Organics and used without further purification. Sinnopal

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TABLE I
Characteristics of the Epoxidized Rubber Latexes Used

Reference latex	Epoxidized unit content (%)	DRC (%)	Proportion of Sinnopa NP 307 (phr)
24.8% ELIR	24.8	20	8
24.6% ELIR	24.6	20	3
24.2% ELIR	24.2	20	2
23.5% ELIR	23.5	20	3
22.8% ELIR	22.8	20	3
21.7% ELIR	21.7	20	3
18.2% ELIR	18.2	20	3
13.3% ELIR	13.3	20	3
5.7% ELIR	5.7	20	3
25.4% ENR	25.4	20	10
23.7% ENR	23.7	20	3
21.9% ENR	21.9	20	3
18.7% ENR	18.7	20	3
9.9% ENR	9.9	20	3
5.7% ENR	5.7	5	3

NP 307 [α -(nohylphenoxy) poly(ethylene oxide)] was purchased from Cognis and used as received without further purification. Benzylamine (Acros Organics) and ammonium diethyldithiophosphate (Acros Organics; purity = 95%) was used as received without further purification. Benzoic acid (Merck) was recrystallized in methanol before use ($F = 122^\circ\text{C}$). 2-Phenylethanol (Prolabo) and dibutylphosphate (DBP) (Acros Organics, purity 97%) were distilled before use. Diethylphosphate (DEP) was prepared by hydrolysis of diethyl chlorophosphate according to the method previously described¹⁰ and then purified by distillation before use [$E_{b_{0.3\text{mmHg}}} = 36\text{--}37^\circ\text{C}$]. Tetramethylammonium benzoate was prepared by neutralization of aqueous solution of benzoic acid by tetramethylammonium hydroxide (Janssen Chimica); after evaporation of solvent, it was dried at 50°C under vacuum. Ceric ammonium nitrate (CAN) (Acros Organics) was dried at 50°C in vacuum before use.

Epoxidation of the rubber latexes

The reaction was carried out in a flask equipped with a mechanical stirrer and a condenser, according to the method previously described.¹² Theoretical levels of epoxidized units were calculated according to the relation: $r_t = [\text{H}_2\text{O}_2]/[\text{Polyisoprene units}]$. The concentrated latex was brought to lower DRC (NR latex was stirred for 8 h at room temperature to eliminate ammonia; LIR-700 latex was directly used). Sinnopal NP 307, as nonionic surfactant, was used to stabilize the latex. Formic acid and hydrogen peroxide were used in equimolar quantities. Epoxidations were performed at 60°C . Several epoxidized rubber latexes were prepared from LIR-700 latex (ELIR) and NR latex (ENR) (Table I).

Reactions of nucleophilic reagents with the epoxidized rubber latexes

The reactions were performed with 23.5% ELIR and 23.7% ENR, respectively. Epoxidized rubber latex (1g) was placed in a Pyrex glass tube equipped with a magnetic stirrer and closed with a screwed stopper with a joint of sealing covered with Teflon. The mixture was stirred in a thermostated bath. An equimolar amount of nucleophilic reagent compared with the epoxidized 1,4-polyisoprene units was then slowly introduced in the latex. The polymer was precipitated with methanol washed with water and methanol, respectively. It was purified by dissolution/precipitation using the system dichloromethane/methanol. Finally, the polymer was dried under vacuum and then analyzed.

Reaction of benzylamine

The pH of the epoxidized rubber latex was previously brought to 8–9 by addition of ammonia solution. Benzylamine was then added drop by drop in the latex maintained at 30°C , and the reaction was prolonged for 48 h.

Reaction of benzoic acid

The reactions were first performed at 25°C without a catalyst and then in presence of tetramethylammonium benzoate (10% compared with epoxidized 1,4-polyisoprene units).

Reaction of 2-phenylethanol

Ceric ammonium nitrate used as catalyst was added to the latex (10% compared with epoxidized 1,4-polyisoprene units). 2-Phenylethanol was then slowly added to the mixture maintained at 30°C , and the reaction was prolonged for 24 h.

Reaction of ammonium diethyldithiophosphate

The reactions were performed at 30°C for 48 and 168 h, respectively.

Reactions of DBP with the epoxidized rubber latexes

The epoxidized rubber latex (60 g DRC 20%) was placed in a thermostated glass cell equipped with a condenser, a temperature probe, and a magnetic stirrer. The temperature of the magnetically stirred latex was raised to 30°C , and then an equimolar quantity of DBP compared with the epoxidized units was added at a constant rate by using the dosimeter of a pH meter. Continued control of the latex pH was per-

formed during the reaction. Samples were taken at different times. The modified rubber contained in each sample was precipitated in methanol and then washed successively with water and methanol. It was purified by dissolution/precipitation with the coupled dichloromethane/methanol. Finally, it was dried at 50°C under vacuum until constant weight and then analyzed.

Measurements

NMR spectra were recorded on a Bruker AC 400 Fourier-transform spectrometer, at 400.13 MHz for ^1H , at 161.98 MHz for ^{31}P , and at 100.61 MHz for ^{13}C . Samples were analyzed in solution in deuterated chloroform-D (99.8% purity; Spectrométrie Spin et Techniques) or methanol-D. In ^1H and ^{13}C NMR, the chemical shifts are expressed in ppm in the δ scale, compared to the singlet of tetramethylsilane (TMS), as the internal standard. In ^{31}P NMR, the chemical shifts of various phosphorus atoms are expressed in the δ scale, with reference to the phosphoric acid peak as the external standard.

IR spectra were recorded on a Fourier-transform Bruker IFC 66 spectrometer in the 4,000–500 cm^{-1} range (liquid film samples were analyzed between two KBr or NaCl cells, and solid ones were analyzed in KBr pellets).

The progress of latex destabilization was followed by turbidimetry using a retrodiffusion IR spectrometer with vertical scanning (Turbiscan MA 1000 from Coulter - Formulaction). Latex sample (4–5 mL) were taken and immediately introduced in the tube of the Turbiscan and then were analyzed at room temperature over 11 days maximum in the case of the most stable latexes. The sample scanning was performed in less than 20 s: the curves obtained represent the variation of retro-diffusion all along the tube containing the sample.

RESULTS AND DISCUSSION

The reactivity of nucleophilic reagents toward epoxidized 1,4-polyisoprene latexes was studied. The objective was to determine whether the nucleophilic reagents that were shown to be able to add onto the epoxidized units of epoxidized rubbers in solution^{5–10} could also react with the same polymers in latex conditions. The study was achieved with ENR latexes, but also with ELIR latexes coming from LIR-700 latex, a synthetic rubber latex prepared by emulsification of a synthesized 1,4-polyisoprene. ELIR latexes were considered to be models of ENR latexes. The compositions of modified rubbers obtained in latex medium were determined by comparison with that of the phosphorylated rubbers prepared in solvent.^{5–10} After a preliminary study performed with various nucleophiles

to verify their ability to react onto epoxidized rubbers in latex medium, a systematic study was achieved with DBP, which was shown to be very reactive in these conditions.

Epoxidation

Epoxidation of rubber latexes was performed with performic acid generated *in situ* from the reaction of hydrogen peroxide with formic acid. An optimization of the epoxidation in latex medium was previously achieved to obtain stable epoxidized rubber latexes and selective epoxidation, by studying the influence of each reaction parameter (such as the nature and the quantity of surfactant used, the temperature, and the quantities of formic acid and hydrogen peroxide used to form performic acid).¹² NR and LIR-700 latexes were stable in the presence of formic acid after the addition of 3–5 phr of nonionic surfactant (polyoxyethylene α -nonylphenyl ether). These stabilized latexes could be successfully subjected to subsequent *in situ* epoxidation. On the whole, at the same epoxidation conditions, the results obtained with LIR-700 and NR latexes were shown to be very similar. The main difference was noted when the reaction was carried out without surfactant addition. In this case, contrary to NR latex that immediately coagulates when formic acid is added (because of overpassing the isoelectric point at pH 4.7), the epoxidation takes place with LIR-700 latex. This result was explained by the fact that the synthetic polyisoprene latex already contained surfactants added to make it stable. Finally, it was concluded that LIR-700 latex could be considered to be a convenient model of NR latex able to be used later to develop new chemical reactions in latex medium.

Optimized epoxidation conditions leading to stable epoxidized polyisoprene latexes and selective epoxidation reactions occurring without secondary processes can be reached when the latexes previously stabilized with 3 phr of a nonionic surfactant (Sinnopal NP 307 for example) are epoxidized at a temperature of 60°C with equimolar quantities of formic acid and hydrogen peroxide. Using these optimized conditions, various epoxidized rubber latexes coming from NR and LIR-700 latexes were prepared (Table I).

Ring opening of oxiranes

Following the epoxidation, the ring opening of the epoxidized rubber oxiranes by action of nucleophilic reagents was thus considered in latex medium. The reagents that were previously shown to be able to react in organic solution with epoxidized rubber (such as amines, carboxylic acids, alcohols, phosphonic and phosphoric acid reagents)^{5–10} were considered. The reactions were performed simultaneously with ELIR

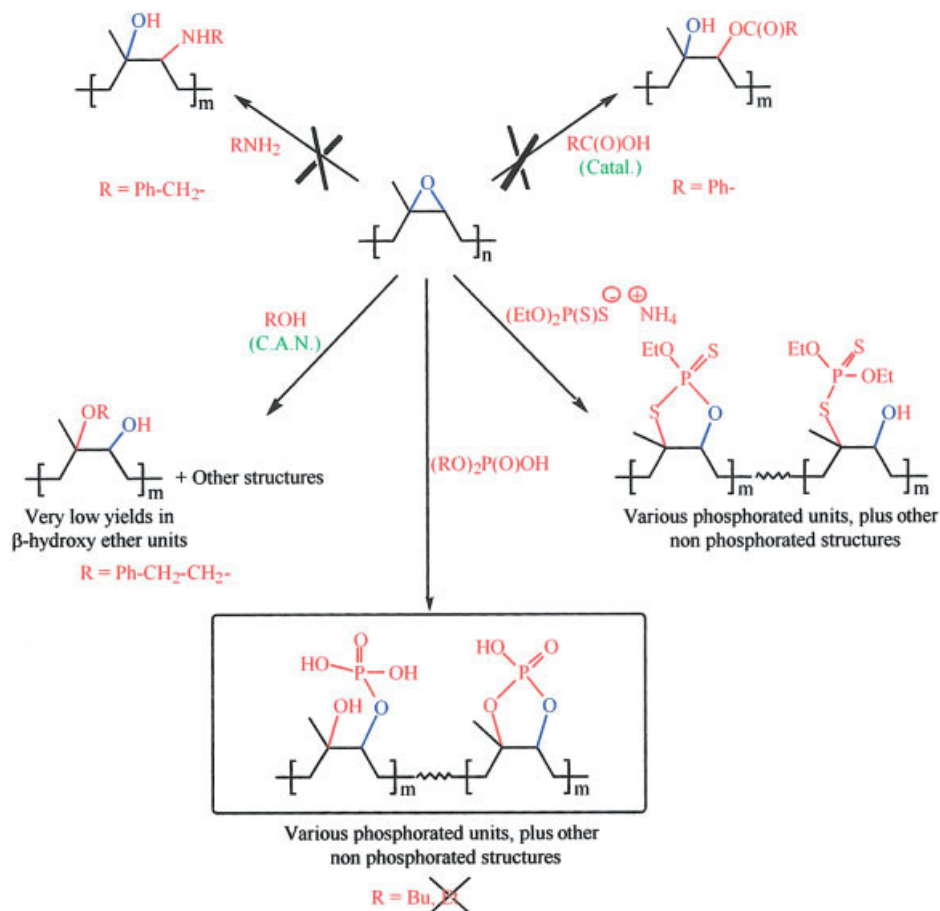


Figure 1 Summary of the results obtained after reaction of nucleophilic reagents with epoxidized rubber latexes performed at 30°C for 48 h.

and ENR latexes at low temperature (30°C) for 48 h (Fig. 1). No reaction was observed with benzylamine and benzoic acid, respectively chosen as amine and carboxylic acid reagents. On the other hand, positive results were obtained with the other reagents, more especially with the phosphorated reagents. Because DBP led to the most significant results, this last reagent was selected to continue the study to obtain a better understanding of the oxirane ring opening of epoxidized rubbers in latex medium.

To verify the ability of DBP to react with oxirane rings of epoxidized rubber in latex medium, the re-

sults obtained in these conditions were compared with those obtained in organic solvent.^{10,13} In dichloromethane and without an external catalyst, DBP reacts quickly with partially epoxidized 1,4-polyisoprene: epoxidized units are totally consumed after only 3 h (Fig. 2). The reaction is autocatalyzed by the P—OH acid functions of the reagent,¹⁴ and the oxirane ring is activated through the formation of a hydrogen-type bond with the acid function of the reagent,¹⁵ which makes the oxirane more electrophilic. DBP adds itself onto the oxirane ring, more especially according to an α -addition, to lead to a β -hydroxyphosphate

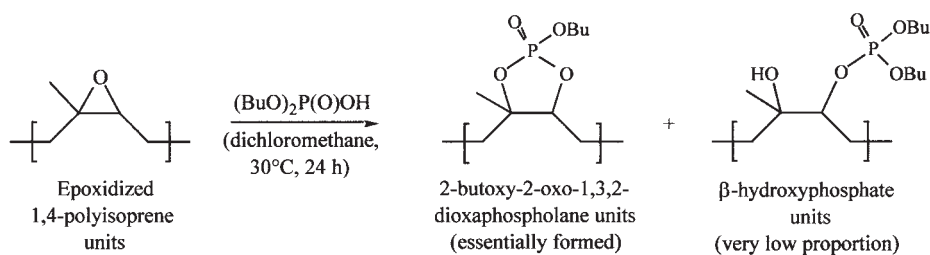


Figure 2 Various units formed after reaction of DBP with epoxidized 1,4-polyisoprene in solution.

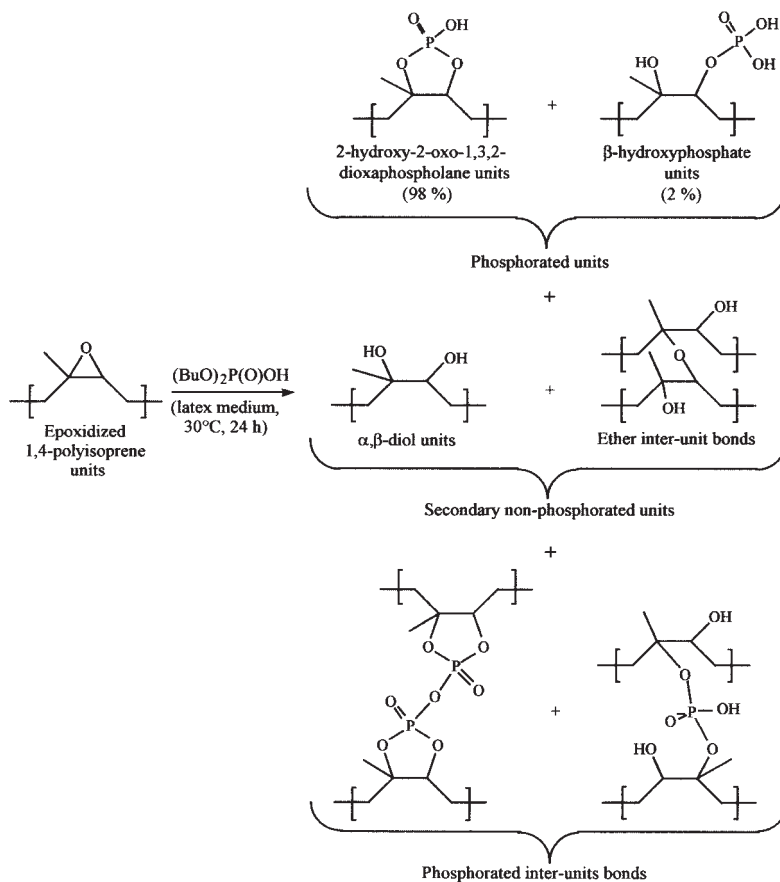


Figure 3 Various units formed after reaction of DBP with ELIR latex.

structure. Due to their high reactivity, β -hydroxyphosphates formed according to α -addition are immediately transformed in 2-butoxy-2-oxo-1,3,2-dioxaphospholane. The transformation of β -hydroxyphosphates resulting from a β -addition (minority) is much slower. In the same conditions as in organic medium, the reaction of DBP with partial ELIR latex (21.7% ELIR latex) occurs faster (Figs. 3 and 4), but with slight differences. β -Hydroxyphosphate and 2-oxo-1,3,2-dioxaphospholane units are also formed but in their acidic form, and secondary processes leading essentially to the formation of phosphorated and nonphosphorated inter-unit bonds are noted.¹³ As for the reaction performed in solution, the addition of the dibutylphosphate group can occur in either the α or the β position of the oxirane, with the addition in α position being highly favored. The β -hydroxyphosphate formed by α -addition is quickly hydrolyzed and immediately reacts on itself to form a 2-hydroxy-2-oxo-1,3,2-dioxaphospholane unit or with a neighboring epoxidized unit of the same (or other) polymer chain to create a dialkylphosphate type bond that afterward rearranges in 2-hydroxy-2-oxo-1,3,2-dioxaphospholane and α,β -diol units. The β -hydroxyphosphate units formed by β -addition are also quickly hydro-

lyzed and then slowly transformed into 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units.

Study of reaction of DBP with ELIR latexes

Reaction of DBP with ELIR latexes was widely studied to collect information on latex behavior. Various parameters were successively considered: latex pH, surfactant concentration, DBP concentration, epoxidation rate of the polyisoprene contained in the latex, and rate of introduction of DBP into the ELIR latex. The influence of reaction temperature was not studied here because DBP addition on oxirane rings of epoxidized polyisoprene can be easily performed at room temperature.⁶ Moreover, preliminary experiments performed in latex conditions have shown that the reaction occurs easily at low temperature (Fig. 1). Consequently, the temperature was kept to 30°C during all of the following experiments.

To study the effect of each parameter, each was varied keeping all others constant.

Influence of latex pH

Before considering the influence of pH on DBP reaction with the epoxidized polyisoprene contained in

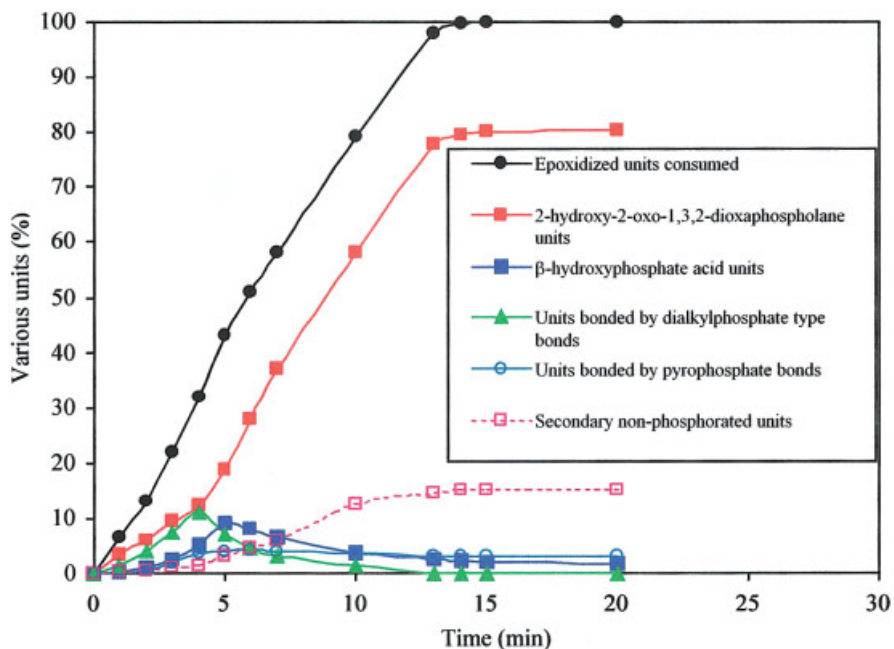


Figure 4 Reaction of DBP with 21.7% ELIR latex. DRC 20%, 3 phr of Sinnopal NP 307, 30°C, $r' = [\text{DBP}]/[\text{epoxidized units}] = 1 \text{ mol}\cdot\text{mol}^{-1}$, rate of DBP addition into the ELIR latex = 3.8 ml.min⁻¹.

the ELIR latex, it was useful to verify the stability of this last according to pH. For that, 21.7% ELIR latex was considered. Its pH measured at 30°C was equal to 1.6. By decreasing it (by addition of formic acid), the latex coagulation occurred at about pH 0.8. On the other hand, no latex destabilization was observed when pH was increased by the addition of ammonia solution. This showed the importance of keeping the latex pH higher than 0.8 during the reaction, to avoid its coagulation. In comparison, the ENR latex containing an ENR of the same epoxidized unit content remained stable when pH was greater than 0.7.

Several reactions were performed (at 30°C, with equimolar quantity of DBP compared with epoxidized 1,4-polyisoprene units) with 21.7% ELIR latex, whose pH was set to 4, 7, 8, and 10, respectively:

- With latex set to pH 10, an increase in pH was noted as the addition of DBP into the latex progressed, but, at the end, the mixture remained basic, and no destabilization of the latex was noted. No transformation of the epoxides occurred, which is not surprising because of the probable neutralization of DBP by ammonia.
- With latex set to pH 7 or 8, latex coagulation was noted during the addition of DBP into the latex.
- With latex set to pH 4, only 10% of the epoxidized units were transformed (5% in 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units; 2% in β -hydroxyphosphate units). The low addition yield is explained by the latex coagulation that occurred

before total introduction of DBP. At this moment, the pH was about 2.6.

- With latex set to pH 1.6 (pH of the latex after epoxidation), the epoxidized units were totally transformed in phosphorated units after 15 min, and no destabilization of the latex was noted.

The latex coagulations observed at pH 0.8 and higher are surprising because it was noted that 21.7% ELIR latex was normally stable at pH 0.8 and higher. The presence of acidic species in the Sinnopal NP 307, as demonstrated by controlling the pH of Sinnopal NP 307 aqueous solutions of different concentrations (Fig. 5), could contribute to improve the latex stability. Therefore, it can be suggested that these acids could be neutralized by the ammonium solution added to set the latex to a higher pH.

Influence of surfactant concentration

To study the influence of surfactant concentration, two series of experiments were performed:

1. Using the same ELIR latex previously epoxidized in the presence of 3 phr of Sinnopal NP 307, and then performing the DBP reaction (Fig. 6).
2. Performing DBP reactions with several ELIR latexes previously prepared in the presence of various quantities of Sinnopal NP 307 (Fig. 7).

In the two series, the reactions were performed at 30°C, by using a molar ratio $r' = [\text{DBP}]/[\text{epoxidized units}] = 1$.

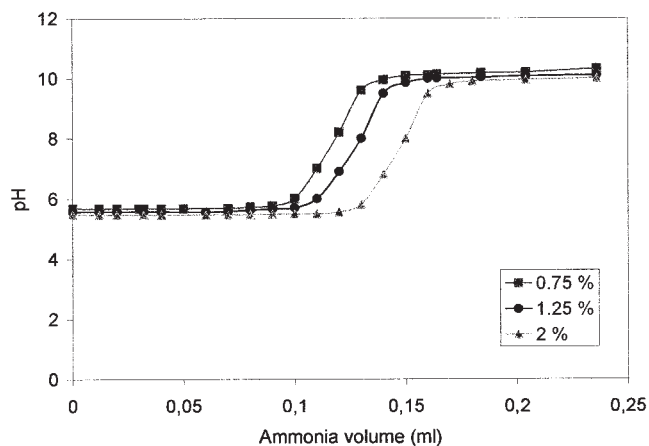


Figure 5 Titration curves obtained after neutralization at 30°C of Sinnopal NP 307 aqueous solutions of different concentrations expressed in g % per L.

In the first series, the results acquired with 22.8% ELIR latex were compared with those obtained with this same latex after addition of, respectively, 2 and 5 phr of Sinnopal NP. No destabilization of 22.8% ELIR was noted with the increase of surfactant concentration. Progress of the epoxidized units, the 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units, and the β -hydroxyphosphate units are related in Fig. 6. Note that the reaction kinetic is accelerated when an additional amount of Sinnopal NP 307 is introduced in the 22.8% ELIR latex. However, this reaction acceleration is kept same and does not vary when the amount of added Sinnopal NP 307 is increased. In the same time, the kinetics of formation of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units [Fig. 6(B)] and β -hydroxyphosphate units [Fig. 6(C)] are also reduced. However, after total consumption of the oxirane rings, that is 15 min [Fig. 6(A)], the contents in 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units (80% of the epoxidized units

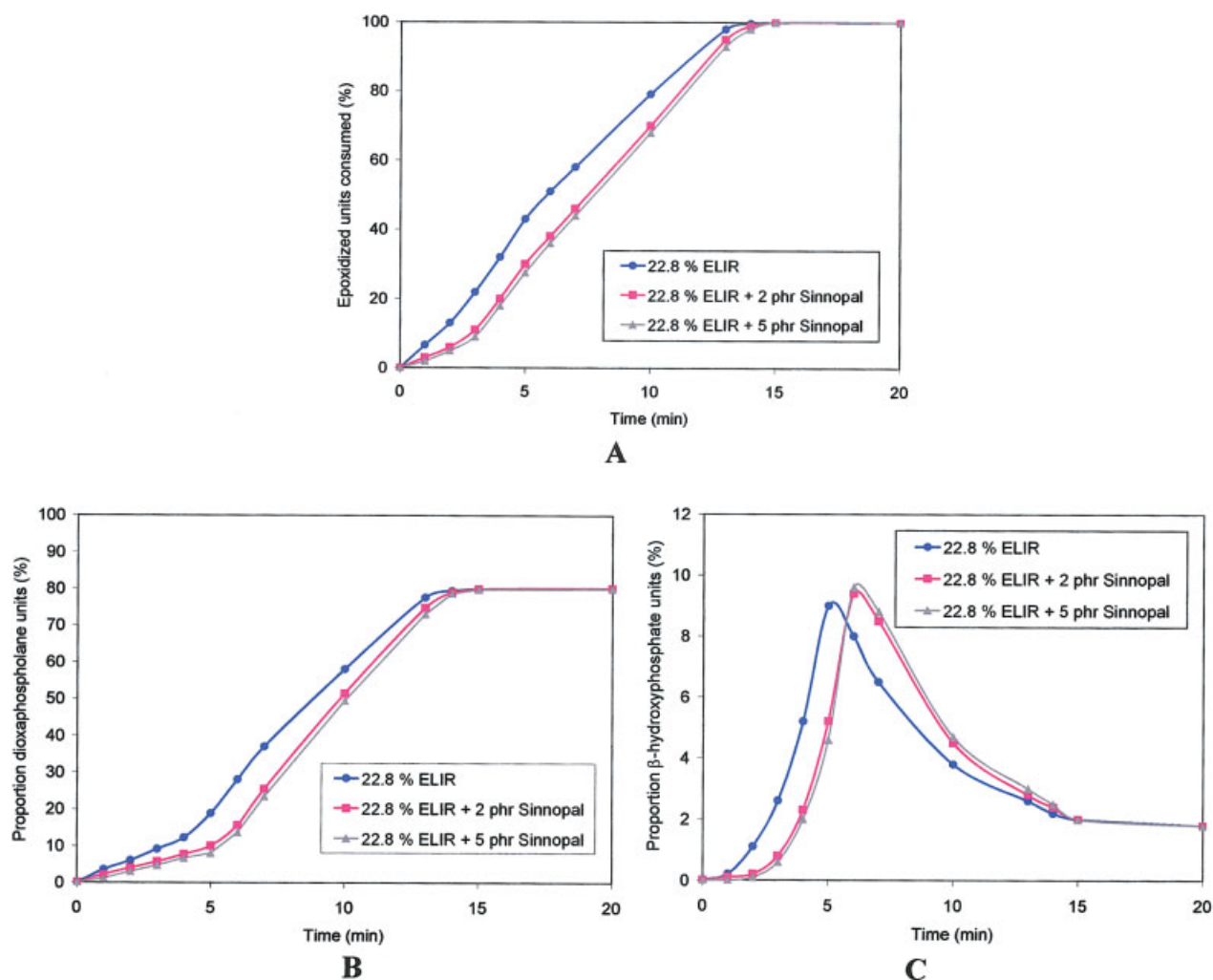


Figure 6 Reaction of DBP with 22.8% ELIR latex according to Sinnopal NP 307 concentration: Study of the case in which the Sinnopal NP 307 was added after the epoxidation stage. (A) Consumption of epoxidized units *versus* time. (B) Progress of dioxaphospholane units *versus* time. (C) Progress of β -hydroxyphosphate units *versus* time. DRC 20%, 30°C, $r' = [\text{DBP}]/[\text{epoxidized units}] = 1 \text{ mol} \cdot \text{mol}^{-1}$, rate of DBP addition into the ELIR latex = $3.8 \text{ ml} \cdot \text{min}^{-1}$.

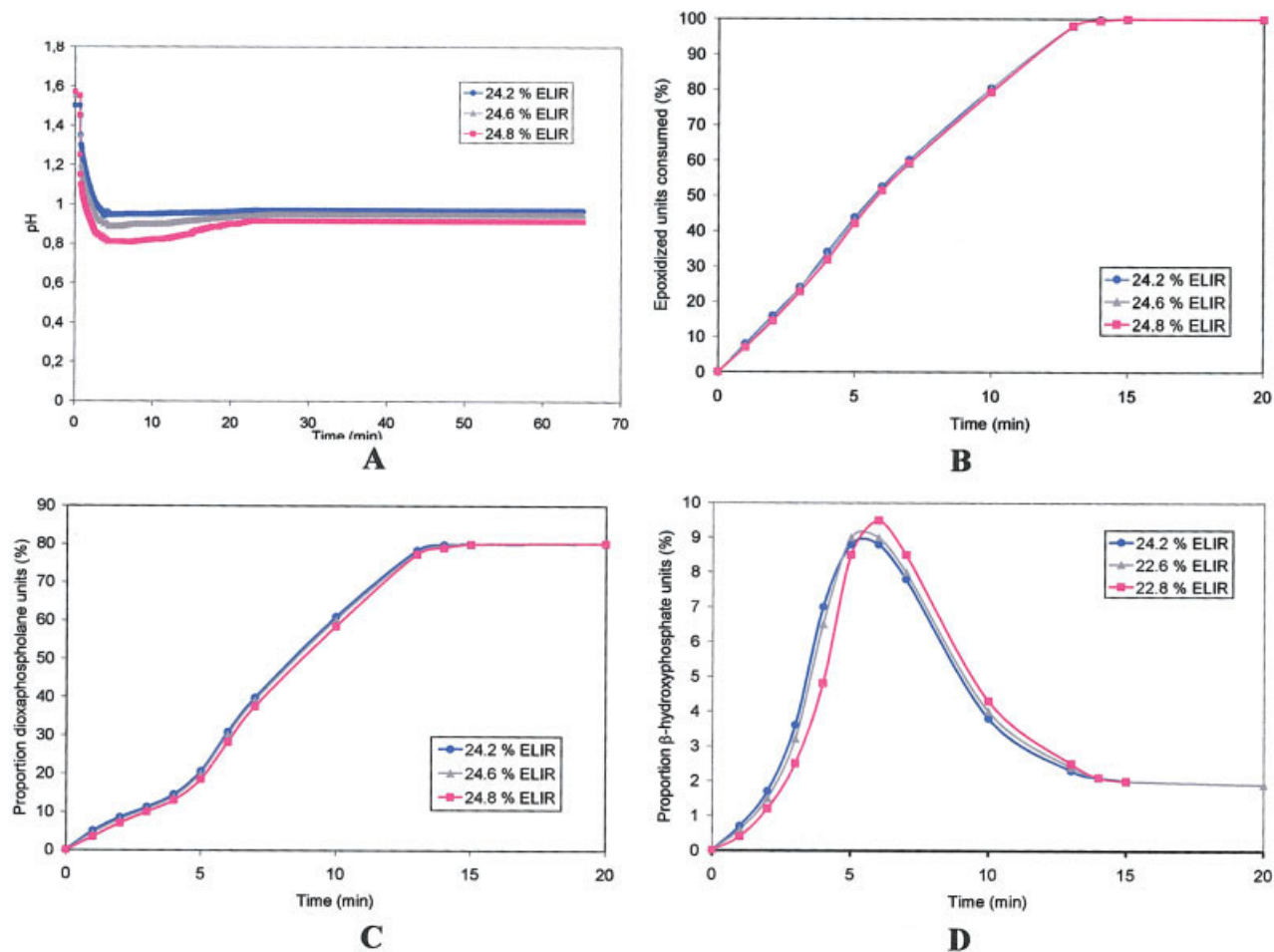


Figure 7 Reaction of DBP with 24% ELIR latex according to Sinnopal NP 307 concentration: Study of the case in which the concentration in Sinnopal NP 307 is set before the epoxidation stage. (A) Progress of pH *versus* time. (B) Consumption of epoxidized units *versus* time. (C) Progress of dioxaphospholane units *versus* time. (D) Progress of β -hydroxyphosphate units *versus* time. DRC 20%, 30°C, $r' = [\text{DBP}]/[\text{epoxidized units}] = 1 \text{ mol}\cdot\text{mol}^{-1}$, rate of DBP addition into the ELIR latex = 3.8 $\text{ml}\cdot\text{min}^{-1}$.

consumed) and β -hydroxyphosphate units (2%) are always the same whatever the quantity of Sinnopal NP 307 added. These proportions correspond to that obtained with 22.8% ELIR latex without additional Sinnopal NP 307. Concerning the formation of β -hydroxyphosphate units, it progresses through a maximum observed after about 5 min (9–10% yield compared with the initial epoxidized units), and then decreases to a 2% constant yield. Moreover, it was noted that the proportion of initial epoxidized units transformed in α,β -diol units and/or in ether bonds (15%), as well as that involved in the formation of pyrophosphate groups (3%), are always the same whatever the Sinnopal NP 307 quantity added. The results obtained here are akin to that observed during the epoxidation performed in latex medium, which also showed a slow down of the epoxidation rate when the Sinnopal NP 307 concentration was increased whereas the final contents of epoxidized units was identical.¹² These results can be explained by a slowdown of DBP pen-

etration inside the particles due to the increase of the surfactant barrier at the particle surface.

The second series of experiments was performed with three ELIR latexes (24.2% ELIR, 24.6% ELIR, and 24.8% ELIR) previously stabilized before epoxidation stage with 2, 3, and 8 phr of Sinnopal NP 307, respectively. No latex destabilization was observed during the introduction of DBP, whatever the latex used. The latex pH progress, the epoxidized unit consumption, and the formation of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane and β -hydroxyphosphate units *versus* time are shown in Fig. 7. At the very beginning of the reaction, the pH decrease is all the more significant as the surfactant concentration is high [Fig. 7(A)], while the kinetics of epoxidized unit consumption [Fig. 7(B)] are practically similar. It is the same for that concerning the kinetics of formation of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane and β -hydroxyphosphate units [Figs. 7(C and D), respectively]. It was also noted that, whatever the Sinnopal NP 307 concentration, the final

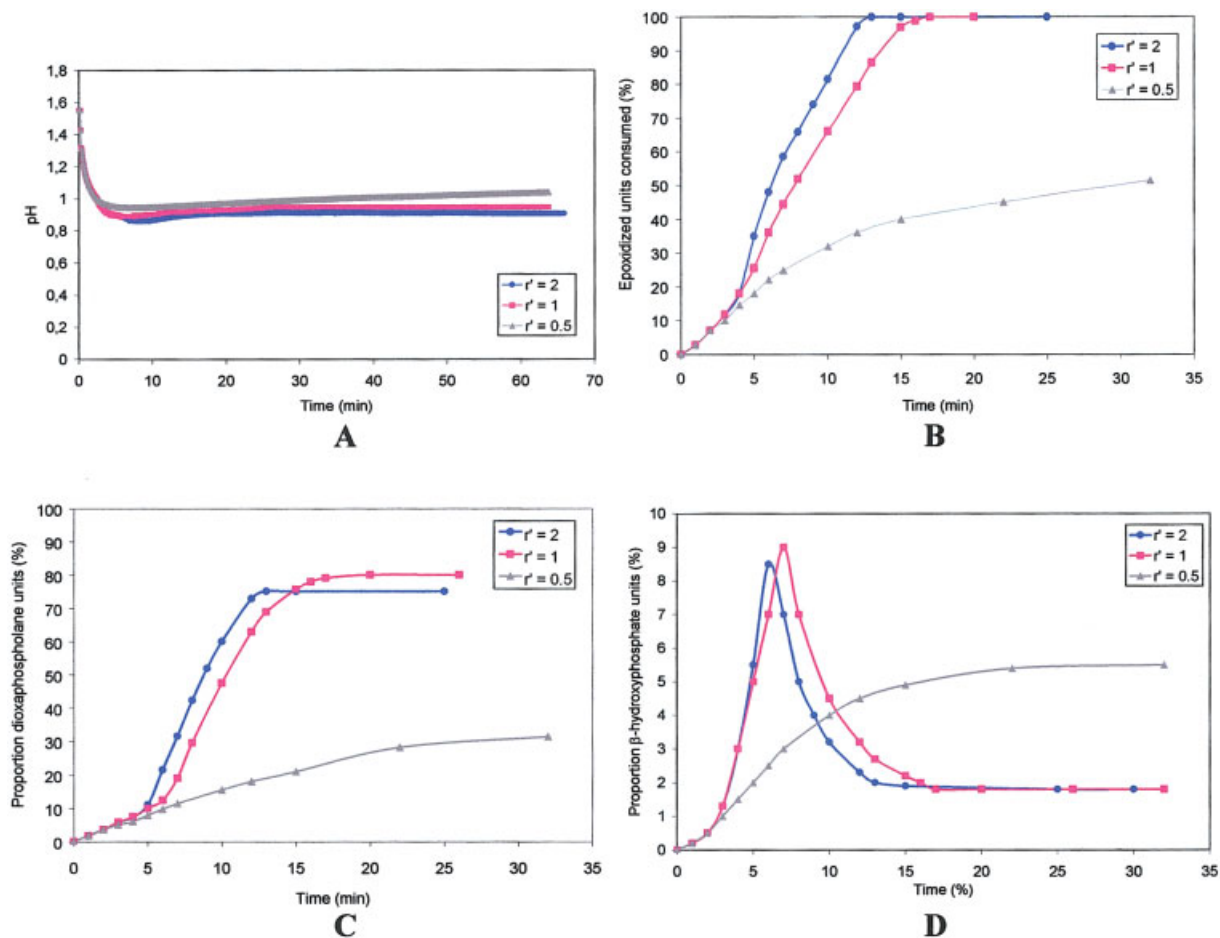


Figure 8 Reaction of DBP with 21.7% ELIR latex according to $r' = [\text{DBP}]/[\text{epoxidized units}]$. (A) Progress of pH versus time. (B) Consumption of epoxidized units versus time. (C) Progress of dioxaphospholane units versus time. (D) Progress of β -hydroxyphosphate units versus time. DRC 20%, 3 phr of Sinnopal NP 307, 30°C, rate of DBP addition into the ELIR latex = 1.2 mL \cdot min $^{-1}$.

compositions of the modified polyisoprene were identical: 80% of epoxidized units converted in 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units, 2% in β -hydroxyphosphate units, 3% in the formation of pyrophosphate groups, and 15% in α,β -diol and/or ether bonds.

Influence of DBP concentration

Several experiments were carried out with 21.7% ELIR using the following molar ratios $r' = [\text{DBP}]/[\text{epoxidized units}] = 2, 1, \text{ and } 0.5$, respectively. The results summarized in Figure 8 show that the epoxidized unit consumption progresses similarly to latex pH. During the first moments of the reaction (between 0 and 5 min), the pH decrease is the same whatever the DBP concentration and in the same time the epoxidized units are consumed at the same rates. After that, the pH drop and the epoxidized unit consumption rate were shown to depend on DBP concentration: both increase with DBP concentration [Fig. 8(B)]. When r'

= 0.5 (ratio corresponding to a DBP concentration twice as low as that of epoxidized units), only half of the epoxidized units are consumed, which shows that the use of DBP in default compared with the initial epoxidized units does not favor the secondary mechanisms.

From a kinetic point of view, the formation of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units is accelerated when DBP concentration is increased [Fig. 8(C)]. On the other hand, at the end of the reaction, the final proportion of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units is higher as the concentration of DBP is low, which demonstrates that the secondary reaction effects are increased with DBP concentration. When $r' > 1$, the β -hydroxyphosphate unit formation progresses through a maximum value, which increases when DBP concentration is increased, but at the end of the reaction the β -hydroxyphosphate unit contents are identical (about 2%) [Fig. 8(D)]. On the contrary, when DBP is used in default in comparison with the epoxidized units, the β -hydroxyphosphate unit content

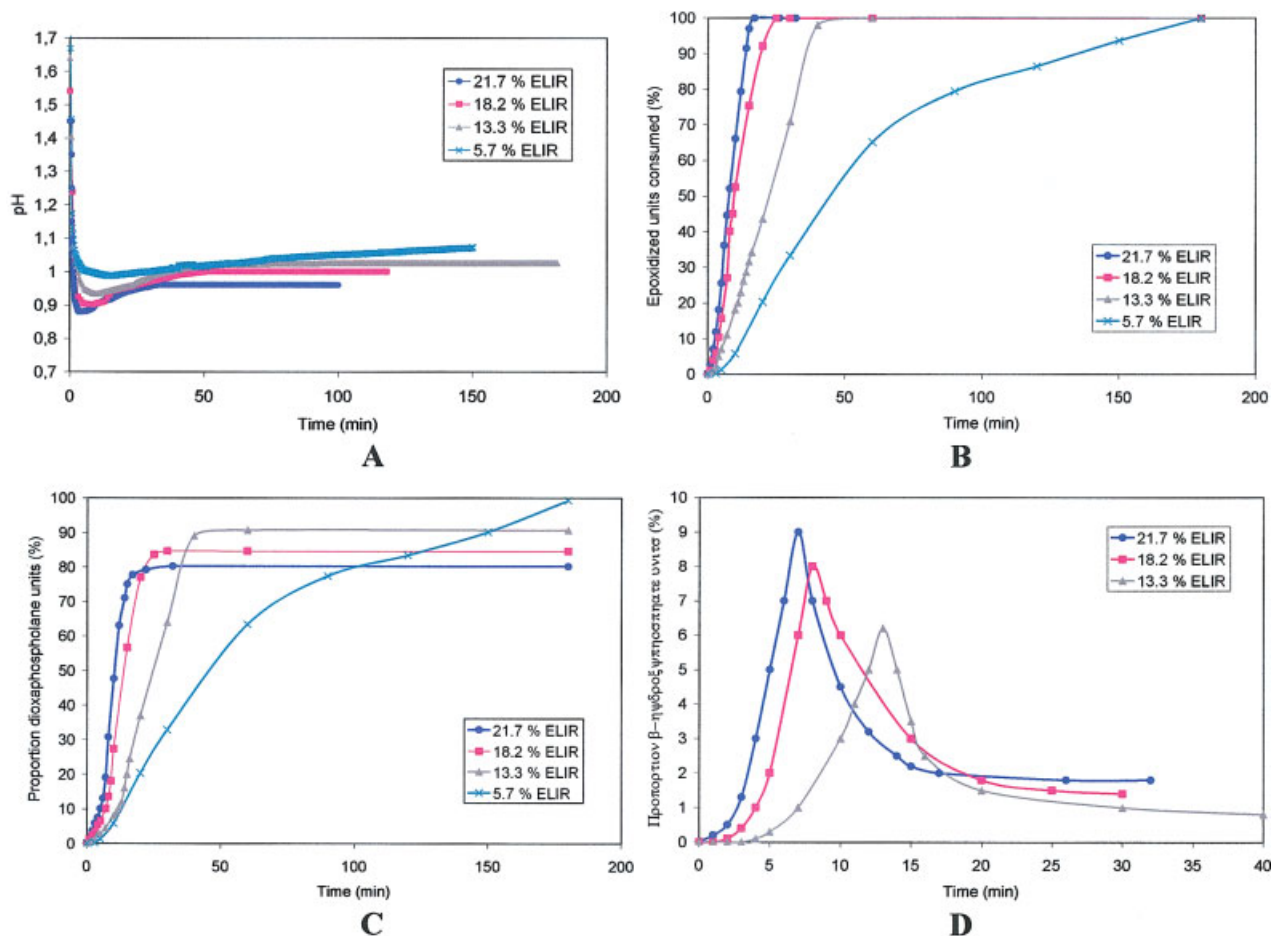


Figure 9 Reaction of DBP with ELIR latex according to the epoxidized unit content in the ELIR. (A) Progress of pH *versus* time. (B) Consumption of epoxidized units *versus* time. (C) Progress of dioxaphospholane units *versus* time. (D) Progress of β -hydroxyphosphate units *versus* time. DRC 20%, 3 phr of Sinnopal NP 307, 30°C, $r' = [\text{DBP}]/[\text{epoxidized units}] = 1 \text{ mol}\cdot\text{mol}^{-1}$, rate of DBP addition into the ELIR latex = $1.2 \text{ ml}\cdot\text{min}^{-1}$.

progresses regularly to reach 5% at the end of the reaction. These results could indicate that the formation of β -hydroxyphosphate coming from β -addition would be favored at low DBP concentrations, more especially at DBP concentrations lower than those of epoxidized units.

These results showed that DBP addition yield highly depends on DBP concentration. It is optimum when the reaction is performed with an equimolar quantity of DPB compared with epoxidized units. The possibility of performing partial modifications of the epoxidized units in latex medium without consequence on DBP addition yields is also very interesting.

Influence of the epoxidized unit content of the ELIR

Four ELIR latexes having various epoxidized unit contents were considered: 5.7% ELIR, 13.3% ELIR, 18.2% ELIR, and 21.7% ELIR, respectively. Their coagulation according to pH was previously followed, showing that it occurs always at pH 0.8. The results of the

present study are summarized in Figure 9. The curves of pH variations *versus* time [Fig. 9(A)] show that the pH decrease at the beginning of the reaction is all the more significant as the epoxidized unit content of the ELIR is high. At the end of the reaction, this pH order in relation to the initial epoxidized unit content of the ELIR is kept unchanged. This result is logical due to the fact that the pH of the latex decreases when the epoxidized unit content is increased. Moreover, because the reactions were always performed using equimolar quantities of DBP compared with the epoxidized units, the concentration of DBP in the latex is all the higher as the epoxidation level of the ELIR in the latex is high.

Concerning the epoxidized unit consumption [Fig. 9(B)], it is all the faster as the epoxidized unit content of the ELIR is high. For instance, 15 min is enough to consume the totality of the epoxidized units contained in 21.7% ELIR latex, as 3 h are necessary for the 5.7% ELIR latex. These results are comparable with those of the epoxidation performed in latex medium that also

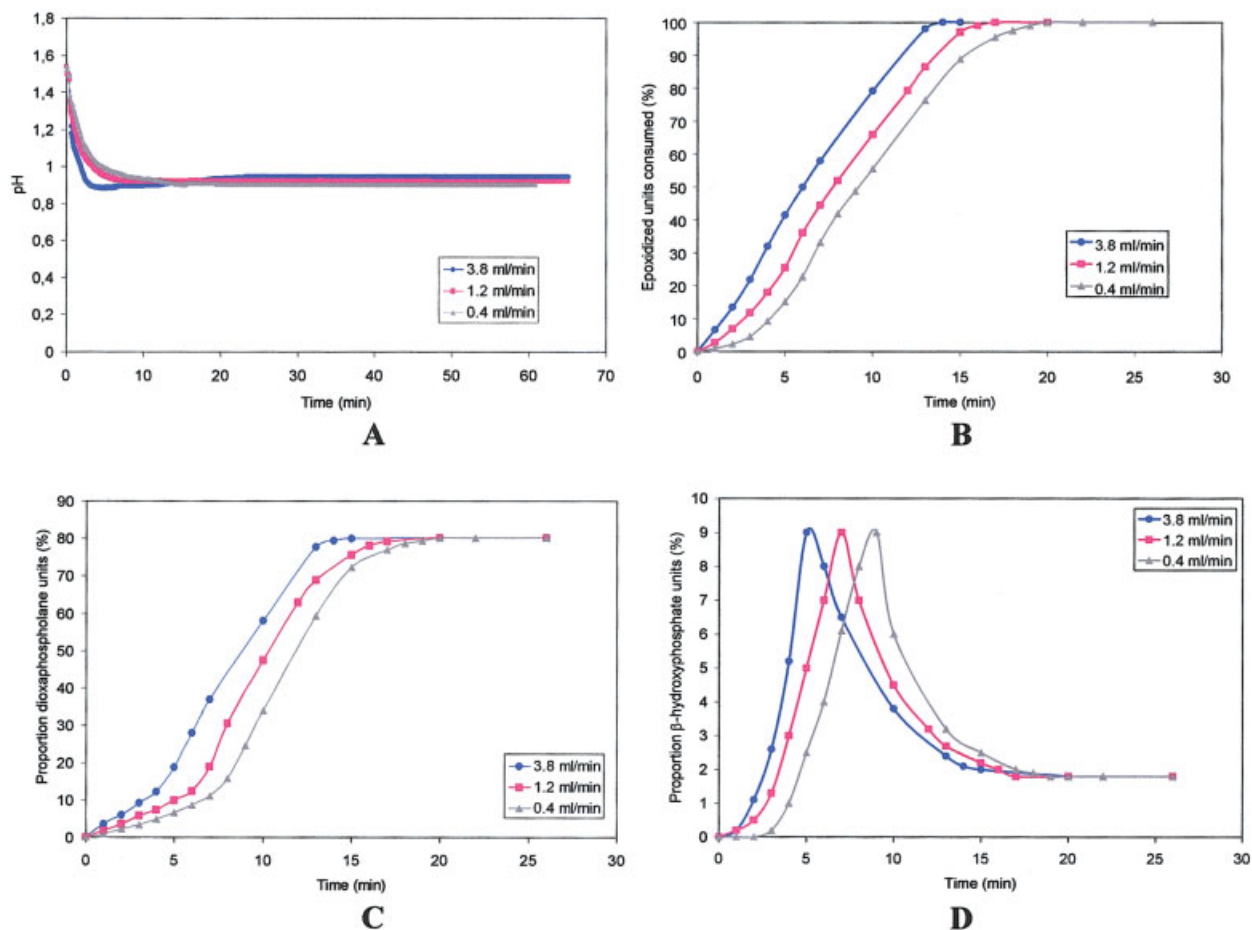


Figure 10 Reaction of DBP with 22.8% ELIR latex according to the rate of DBP addition into the ELIR latex. (A) Progress of pH *versus* time. (B) Consumption of epoxidized units *versus* time. (C) Progress of dioxaphospholane units *versus* time. (D) Progress of β -hydroxyphosphate units *versus* time. DRC 20 %, 3 phr of Sinnopal NP 307, 30°C, $r' = [\text{DBP}]/[\text{epoxidized units}] = 1 \text{ mol} \cdot \text{mol}^{-1}$.

showed an increase of the epoxidation rate with the theoretical content set.¹² In the same time, the rates of formation of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane and β -hydroxyphosphate units are accelerated when the epoxidized unit content in the ELIR is increased [Figs. 9(C and D), respectively]. However, after complete consumption of the epoxidized units, the proportions of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units are all the lower as the epoxidized unit content of the ELIR in the initial latex is high. It is the contrary for those concerning the proportions of β -hydroxyphosphate, but they represent less than 2% of the epoxidized units transformed (not characterized with 5.7% ELIR latex: no signal at $\delta = 1.63 \text{ ppm}$ in ^{31}P NMR). The proportions of pyrophosphate groups progress also similarly to that of β -hydroxyphosphate: 3% of the epoxidized units consumed for the 21.7% ELIR latex, 2% for 18.2% ELIR, traces for 13.3% ELIR, and 0% for 5.7% ELIR). In summary, the yield of transformation of epoxidized units in phosphorated units is all the higher as the epoxidized unit content in the ELIR is low. These results are explained by the

effects of the secondary reactions that transform part of the epoxidized units in nonphosphorated ones. They represent 15% of the epoxidized units consumed for 21.7% ELIR latex, 12% for 18.2% ELIR, 5.5% for 13.3% ELIR, and 0% for 5.7% ELIR.

Influence of the rate of DBP addition into the ELIR latex

Several experiments were performed with 22.8% ELIR latex using various rate of DBP introduction (3.8, 1.2, and 0.4 $\text{ml} \cdot \text{min}^{-1}$). The results are given in Figure 10. By increasing the rate of DBP addition into the ELIR latex, the drop of pH at the very beginning of the reaction is accelerated, but after about 20 min it tends to be stabilized to the same value [Fig. 10(A)]. For the rates considered here, the pH does not fall under the fateful value 0.8, which explains why the latexes remain stable at the end of the reaction, but, when higher rates are used, the coagulation can occur. The coagulation risks are favored when the rate of addi-

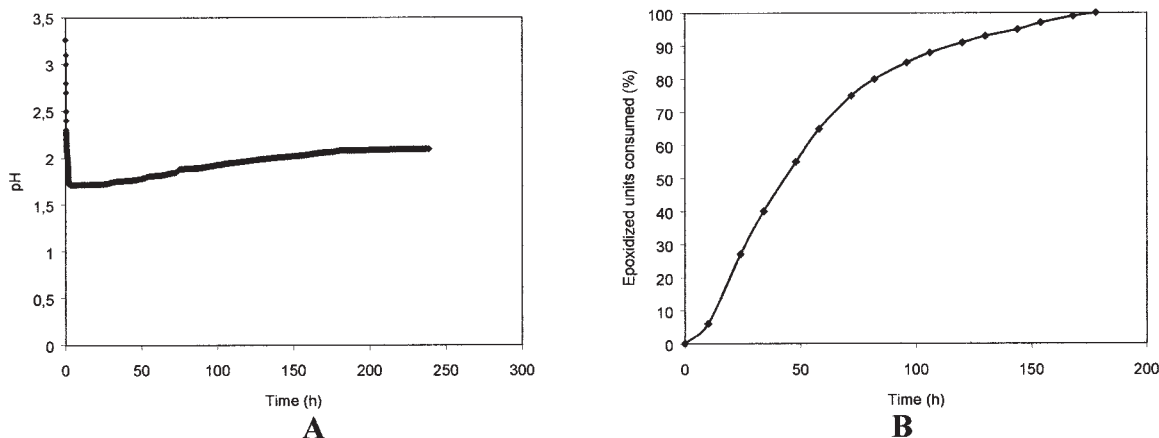


Figure 11 Reaction of DBP with 5.7% ENR latex: (A) Progress of pH *versus* time. (B) Consumption of epoxidized units *versus* time. DRC 5%, 3 phr of Sinnopal NP 307, 30°C, $r' = [\text{DBP}]/[\text{epoxidized units}] = 1 \text{ mol}\cdot\text{mol}^{-1}$, rate of DBP addition into the ENR latex = $0.01 \text{ ml}\cdot\text{min}^{-1}$.

tion of DBP into the latex is increased, but can be also limited by decreasing the latex DRC.

The kinetic of the reaction also depends on the rate of addition of DBP into the latex. The rate of epoxidized unit consumption increases when the addition of DBP is increased (the epoxidized units are totally consumed after 14 min at a DBP addition rate of $3.8 \text{ ml}\cdot\text{min}^{-1}$, against 20 min at $0.4 \text{ ml}\cdot\text{min}^{-1}$) [Fig. 10(b)]. As a consequence, the rates of formation of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane and β -hydroxyphosphate units follow the same way (Figs. 10(c and d), respectively). On the other hand, the final proportions of the two types of units are the same whatever the rate chosen for the addition of DBP into the latex.

Study of reaction of DBP with ENR latexes

The first experiments performed with various ENR latexes (Table I) according to the conditions previously optimized with ELIR latexes (at 30°C, with $[\text{DBP}]/[\text{epoxidized units}] = 1$) showed a rapid latex coagulation when DBP addition was carried out at a rate of 0.4 or $0.05 \text{ ml}\cdot\text{min}^{-1}$. On the other hand, when the rate of introduction of DBP was reduced to $0.01 \text{ ml}\cdot\text{min}^{-1}$, the latex stability was prolonged, thus permitting the reaction to occur. For example, with 21.9% ENR latex, the latex coagulation was noted after 12 h (time necessary to add DBP at a rate of $0.01 \text{ ml}\cdot\text{min}^{-1} = 7 \text{ h}$), and the reaction could occur. At this rate of $0.01 \text{ ml}\cdot\text{min}^{-1}$, stable phosphorated latexes could be prepared under the condition using ENR latexes having low epoxidized unit contents (about 5%) and to dilute the latex to a DRC 5%. Under these soft conditions, the latex pH was always maintained higher than 1.7 (Fig. 11). As a consequence, the reaction rate was shown to be

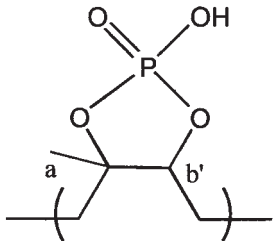
significantly slower, since 180 h was necessary to consume the totality of the epoxides (Fig. 11). As with the ELIR latex containing ELIR of same epoxidized unit content, only 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units were characterized by ^1H and ^{31}P NMR (Table II). Their proportion corresponds to the rate of epoxidized units consumed.

Characterization of the stability of the various latexes

The stability of the latex coming from the chemical modification of 21.7% ELIR latex by DBP (PLIR) was followed using Turbiscan (see Experimental). The curves relating the variations of retrodiffusion *versus* time show a retrodiffusion decrease in the bottom of the tube (Fig. 12). This behavior, similar to that observed with LIR-700 latex and ELIR latexes, translated a phenomenon of creaming and particle aggregations (reversible phenomenon). However, the creaming rate of 21.7% PLIR latex prepared from the reaction of DBP with 21.7% ELIR latex is faster than that of LIR-700 latex, as well as that of the other latexes coming from the latter (LIRSU latex: LIR-700 latex stabilized with 3 phr of Sinnopal NP 307; 21.7% ELIR latex) (Fig. 13), which indicates a weakened stability.

Like phosphorated latexes derived from ELIR latex, the latex coming from the chemical modification of 5.7% ENR latex with DBP (PNR) destabilizes itself over time according to creaming and particle aggregations (Fig. 14). As for the phosphorated latexes coming from the LIR-700 latex, its stability is lower than that of initial NR latex (NR) and the other latexes derived from this last (NRSU latex: NR latex stabilized with 3 phr of Sinnopal NP 307; 5.7% ENR latex) (Fig. 15). However, the stability order of the various latexes prepared from NR latex is different from that noted with the latexes derived from LIR-700 latex.

TABLE II
 ^1H and ^{31}P NMR Characteristics of the Phosphorated Units Formed after Addition of DBP onto Epoxidized Units of 5.7% ENR Latex

Structures	^1H NMR		^{31}P NMR
	Protons	δ (ppm)	
 dioxaphospholane	a b'	1.40 4.18	$\delta=16.00\text{ppm}$

CONCLUSION

The reactivity of some nucleophilic reagents [dibutylphosphate (DBP), ammonium diethyldithiophosphate, and to a lesser degree primary alcohols] toward epoxidized 1,4-polyisoprene in latex medium was highlighted. DBP reaction with epoxidized units in latex conditions was shown to be particularly efficient. Compared to that performed in a solvent,¹³ DBP reaction with epoxidized polyisoprenes in latex medium is very fast. However, the reaction progresses differently and is more complex. While in solvent only two kinds of phosphorated units are formed (2-butoxy-2-oxo-1,3,2-dioxaphospholane coming from α -addition, and β -hydroxyphosphate coming from β -addition) supplementary mechanisms occur in latex medium. This result is in part explained by the acidity of the latex

medium, which can justify more particularly the formation of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane cycle (coming from α -addition), acidic β -hydroxyphosphate (coming from β -addition), pyrophosphate groups, α,β -diols, and/or ether bonds.

A systematic study of DBP reaction with ELIR latex (coming from LIR-700 latex) was performed to define how and under what conditions, stable phosphorated latexes could be prepared. Stable phosphorated synthetic latexes could be obtained whatever the epoxidation rate of the initial ELIR latex, but the rate to which DBP is introduced into the latex must be perfectly controlled to avoid the latex coagulation. Partial modification of epoxidized units was also achieved without problem. On the other hand, the importance of latex pH on the reaction progress was highlighted. It was noted that the yield of DBP addition on epoxy-

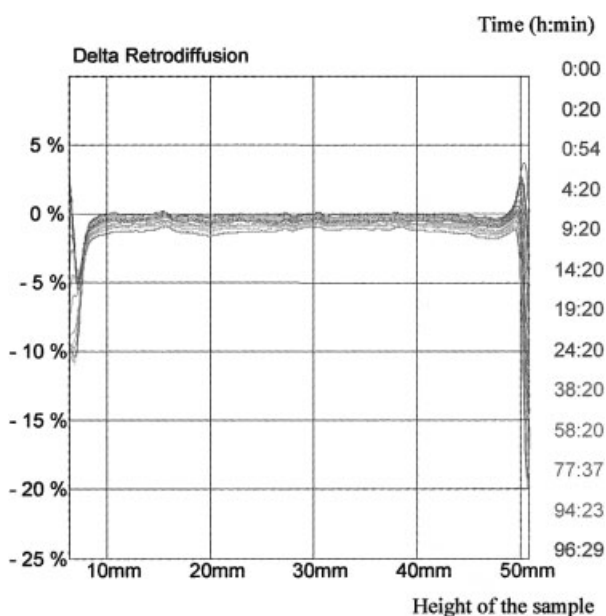


Figure 12 Destabilization of 21.7% PLIR latex coming from DBP reaction with ELIR latex (DRC 20%).

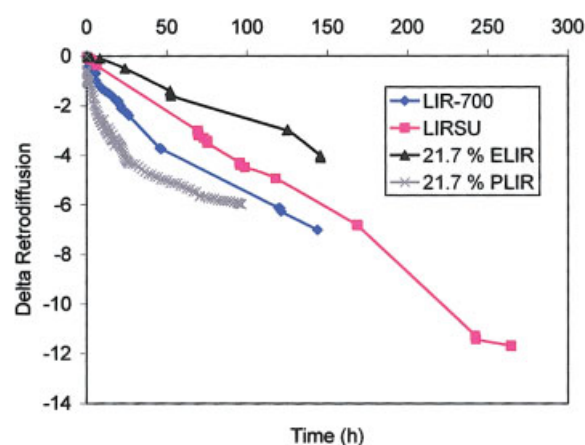


Figure 13 Creaming rates of the various latexes prepared from LIR-700 latex: Initial synthetic polyisoprene latex (LIR-700), LIR-700 latex stabilized with 3 phr of Sinnopal NP 307 (LIRSU), 21.7% epoxidized LIR-700 latex (21.7% ELIR), and 21.7% phosphorated LIR-700 latex coming from DBP reaction with ELIR latex (21.7% PLIR). Measures performed at the bottom of the tube containing the sample (between 6.2 and 9.2 mm).

dized units is highly dependent on the medium acidity (the lower the pH is, the faster the addition rate is, but the pH decrease cannot be lower than 0.8, a limit to keep the stability of the modified latex coming from 22% ELIR latex), but also on the [DBP]/[epoxidized units] molar ratio and on the rate of DBP introduction in the latex.

The reaction of DBP with ENR latexes was shown to be more difficult because of the lower stability of resulting latexes, which necessitates the use of very soft conditions to avoid rubber coagulation. However, stable phosphorated natural rubber latexes could be prepared under the condition of using low DRC latexes with low epoxidized unit contents and to carry out the introduction of DBP into the latex very slowly. This behavior divergence between these two latexes comes from their differences in composition, in particular the nature of the water/rubber particles interfaces that make it possible to ensure the stability of latex. Contrary to LIR-700 latex, NR latex, due to its natural origin, incorporates many nonrubber elements, such as bound or unbound proteins, phospholipids, fatty acids, metals, etc. Moreover, its stabilization is mainly provided by the proteins located on the surface of the rubber particles, which are very sensitive to the action of acids and therefore suitable to be

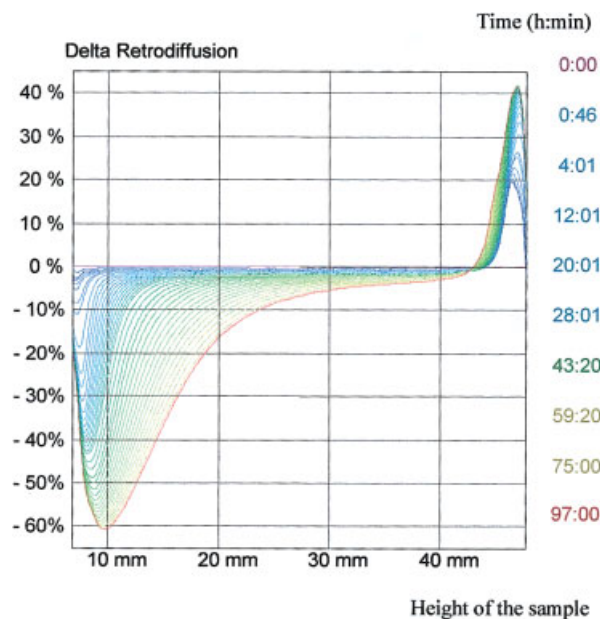


Figure 14 Destabilization of 5.7% PNR latex coming from DBP reaction with ENR latex (DRC 5%).

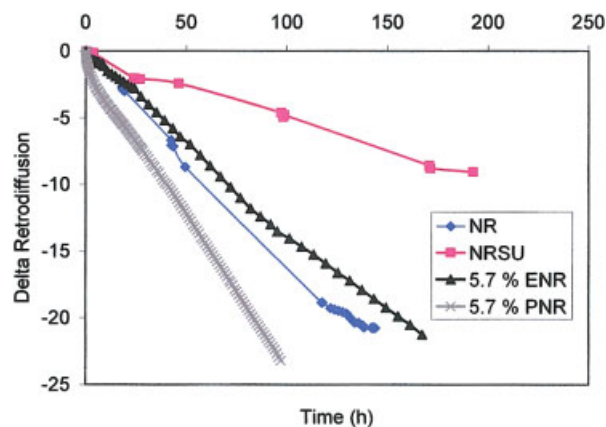


Figure 15 Creaming rates of the various latexes prepared from NR latex: Initial natural rubber latex (NR), NR latex stabilized with 3 phr of Sinnopal NP 307 (NRSU), 5.7% epoxidized NR latex (5.7% ENR), and 5.7% phosphorated NR latex coming from DBP reaction with ENR latex (5.7% PNR). Measures performed at the bottom of the tube containing the sample (between 6.4 and 10 mm).

degraded more or less quickly during a reaction performed at low pH.

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