

Comparative Study of the Epoxidation of Natural and Synthetic Rubber Latices

D. DEROUET*[#], S. MULDER-HOUDAYER* AND J-C. BROSSE*

Epoxidation performed with performic acid generated in situ from the couple hydrogen peroxide/formic acid was studied for synthetic polyisoprene latex (LIR-700) and natural rubber (NR) latex. Various parameters of the reaction (nature and concentration of surfactant used, reaction temperature, and quantities of formic acid and hydrogen peroxide used to form performic acid) were studied and the results obtained for the respective latices were compared. At similar epoxidation conditions, the results obtained with LIR-700 and NR latices were shown to be very close. NR and LIR-700 latices showed the same behaviour during the epoxidation performed with performic acid. Optimal conditions to carry out epoxidation for the preparation of stable latices were also established. This was achieved when the epoxidation was carried out on latices previously stabilised with 3 p.h.r. of a non-ionic surfactant (Sinnopal NP 307[®] for example) at a temperature of 60°C, with equimolar quantities of formic acid and hydrogen peroxide.

Key words: epoxidation; natural rubber latex; synthetic polyisoprene latex; latex stability; epoxidised latices; LIR-700

Chemical modification of natural rubber (NR) has previously been attempted with two objectives in mind to improve the performance of NR in specific applications and to convert NR into a new material that can diversify its traditional uses¹. Epoxidation represents a particularly attractive and convenient method of transforming NR into a new polymer with certain interesting properties. Epoxidised natural rubbers show oil resistance, gas permeability and damping performance². Moreover, from a chemical viewpoint, epoxidised rubbers constitute very interesting intermediates for synthesis because of the reactivity of their oxirane rings toward most nucleophilic reagents^{3,4}. Numerous functional rubbers were synthesized from epoxidised

synthetic or natural rubbers by grafting actives molecules onto oxirane rings by using a SN2 substitution with ring opening, such as reactions with amine⁵, carboxylic acid^{6,7}, alcohol^{8,9}, and phosphoric acid derivatives^{10,11}. However, these products were generally prepared in solution in organic solvents which pose environmental problems. To avoid the use of organic solvents, reaction in the latex medium appears highly desirable.

Latex stage epoxidation has already been studied. From an economic viewpoint, it is much cheaper to epoxidise NR in a latex medium than in an organic solvent¹². Most of the work performed in this field, used peracetic acid or performic acid to epoxidise NR latex^{13–19}

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(Figure 1). The latter peracid is more reactive, but it has to be prepared *in situ* because of its instability²⁰. From an economic viewpoint, the *in situ* performic acid process seems to be more desirable due to the easy availability and the low cost of the reagents²¹. The main problems associated with the *in situ* performic acid route is the formation of various secondary ring-opened and ring-expanded structures: hydrofuran, α,β -diol, β -hydroxyester^{18,22,23}.

As our purpose was to carry out chemistry on epoxidised natural rubber in latex, it was important to have well-defined epoxidised rubber latices. So, our first objective was to optimise the epoxidation of NR carried out with performic acid in the latex state, that is to determine the reaction conditions to improve simultaneously the epoxidation selectivity (suppression of secondary processes) and the stability of the epoxidised latex. Hence the progress of NR latex epoxidation was studied by examining successively the effects of each of the reaction parameters (nature and concentration of surfactants added to improve the latex stability, reaction temperature, reagent concentrations). The aim was also to search for a synthetic latex able to serve as model of NR for our future chemical modification investigations, and so to free ourselves from the problems arising from the presence of non-rubber compounds in NR latex. Thus, the various experiments carried out to optimise the epoxidation of NR latex were simultaneously performed with a synthetic 1,4-polyisoprene latex (LIR-700) prepared

by anionic polymerisation of isoprene. The purpose of this article is to give the results of these comparative investigations.

EXPERIMENTAL

Latex Concentrates

NR latex was a centrifuged field latex of *ca* 60% dry rubber content (DRC), stabilised with ammonia to avoid rubber coagulation. It was composed of *cis* 1,4-polyisoprene (head-tail sequences) plus non-rubber compounds (water, lipids, proteins, carbohydrates, minerals...). Particle diameter in the latex was between 0.01 μm and 5 μm , and the average molecular weight of rubber was $0.25 \cdot 10^6 < M_n < 2.7 \cdot 10^6$ (presence of a gel fraction).

Synthetic polyisoprene latex (LIR-700) was supplied by SIBER-HEGNER. It was prepared by emulsification of a synthetic polyisoprene ($M_n = 29\,000$) having the following chemical structure: 66% *cis* 1,4- units, 27% *trans* 1,4- and 7% 3,4-. It had *ca* 60% DRC, and particle diameter in the latex was about 0.35 μm .

Chemicals

Formic acid and 35% hydrogen peroxide were purchased from Acros, the cationic surfactant (Norianum MC 50®: coco trimethyl ammonium chloride) from CESA, the anionic surfactant (SDS: sodium dodecyl sulphate)

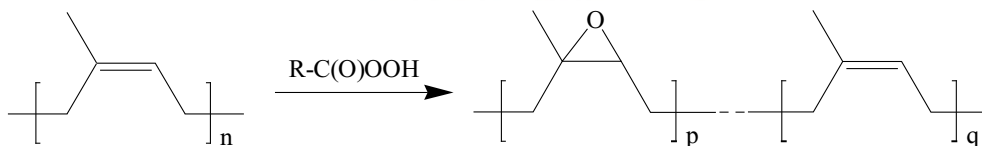


Figure 1. Epoxidation of 1,4-polyisoprenes.

from Acros, and non-ionic surfactants from Cognis (Sinnopal NP 307[®]), Acros (Brij35[®]), Fluka (Brij96[®] and Brij58[®]), Janssen Chimica (Brij30[®]), and Sigma [Brij98[®], Brij56[®] and polyoxyethylene (10) tridecyl ether], respectively. The amphotere surfactant (*N,N*-dimethyl-*n*-lauryl betaine) was synthesized by reaction of sodium monochloracetate (Aldrich) with *N,N*-dimethyl-*n*-laurylamine (Acros) in equimolar quantities. Technical grade solvents (dichloromethane and methanol) were distilled before use. Spectra grade chloroform was purchased from Merck.

Epoxidation Procedure

The reactions were carried out in a flask equipped with a mechanical stirrer and a condenser. The theoretical level of epoxidation was set to 30%. This level was calculated according to the relation: $r_t = (H_2O_2) / (\text{polyisoprene units})$. The concentrated latex was brought to *ca* 20% DRC. NR latex was stirred for 8 h at room temperature to eliminate ammonia. LIR-700 latex was used directly. The latex was stabilised with 2-5 parts of surfactant per hundred of dry rubber (p.h.r.). A determined amount of formic acid was added drop by drop over *ca* 15 min and the mixture was stirred for 15 min. The predetermined amount of hydrogen peroxide was then slowly added (15 min) under continuous stirring.

During the epoxidation, latex samples were taken at various times and isolated by coagulation in methanol. The coagulum formed was washed with water, then several times with methanol, pressed, and finally dried under vacuum at room temperature for 2 days.

¹H NMR Analysis

¹H NMR spectra were recorded on a Bruker AC-200, using 5 mm sample tubes:

$$\frac{I_{(4,70)}}{I_{(5,10)}} = \frac{2(3,4)}{(1,4\text{-}cis) + (1,4\text{-}trans)}$$

$$\frac{I_{(1,70)}}{I_{(1,60)}} = \frac{(1,4\text{-}cis)}{(1,4\text{-}trans) + (3,4)}$$

and CDCl₃ as solvent. The structural composition of the polyisoprene contained in LIR-700 latex was determined using the following relationships:

$$(cis\ 1,4-) + (trans\ 1,4-) + (3,4) = 1$$

$I_{(\delta\ \text{in p.p.m.})}$ represent the signal integrations of the respective protons defined in *Table 1*.

The epoxidised unit contents of epoxidised rubbers in latex samples were determined from ¹H NMR spectra of the isolated epoxidised rubbers¹⁴. For the epoxidised natural rubbers in NR latices, they were obtained from the ratio of the signal integrations corresponding to the protons of carbon-carbon double bonds and oxirane rings, respectively (*Table 2*).

The epoxidation rate was thus given by the relationship:

$$\% \text{ epoxidised units} = \frac{I_{(2,7)}}{I_{(2,7)} + I_{(5,1)}} \times 100 \quad \dots 1$$

For the epoxidised polyisoprenes in synthetic latexes, the 3,4- units were included in the calculation. In this case, the epoxidised unit contents were calculated from the following formula:

$$\% \text{ epoxidised units} = \frac{I_{(2,7)}}{I_{(2,7)} + I_{(5,1)} + I_{(4,7)}} \times 100 \quad \dots 2$$

As the epoxidation process sometimes led to secondary structures, these last were taken into account in the calculation of epoxidation rate. They could be characterised from ¹H NMR spectra (*Table 3*), but when they were in low proportions, IR spectroscopy was used to verify their presence.

IR Analysis

Spectra between 4000 and 500 cm^{-1} were performed using a Perkin-Elmer 1750 spectrometer. The samples were analysed as film form between two NaCl windows. The polyisoprenes contained in the latices are characterised by various vibrations, as shown in Table 4.

After epoxidation of the latices, new vibration characteristics of the oxirane rings were noted (Table 5). The oxiranes in the partially epoxidised 1,4-polyisoprenes are characterised by two vibrations at 1255 cm^{-1} (ν_{CO} symmetrical) and 889 cm^{-1} (ν_{CO} asymmetrical). The vibrations at 3500 cm^{-1} , 1060 cm^{-1} , and 1720 cm^{-1} characterise the secondary structures resulting from ring opening or re-arrangements of oxiranes.

Latex Destabilisation Measurement

The progress of latex destabilisation was followed by turbidimetry using a retro-diffusion IR spectrometer with vertical scanning (Turbiscan MA 1000 from Coulter – Formulacion). 4 mL to 5 mL of latex samples were taken and immediately introduced in the tube of the Turbiscan, then analysed at room temperature within 11 days, maximum in the case of the most stable latices. 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 progress of the epoxidation of NR latex was compared with that of LIR-700 latex,

TABLE 1. RESONANCE ASSIGNMENTS FOR 1,4-POLYISOPRENE UNITS (^1H NMR)

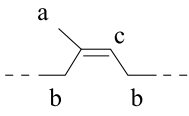
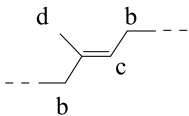
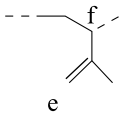
Structures	Protons	Chemical shifts (p.p.m.)
 <i>cis</i> 1,4-	a b c	1.70 2.00 5.10
 <i>trans</i> 1,4-	d	1.60
 3,4-	e f	4.60 and 4.70 2.06

TABLE 2. RESONANCE ASSIGNMENTS FOR EPOXIDISED 1,4-POLYISOPRENE UNITS (^1H NMR)

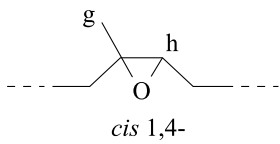
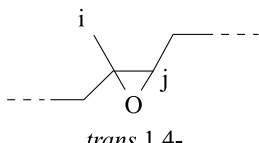
Structures	Protons	Chemical shifts (p.p.m.)
 <i>cis</i> 1,4-	g h	1.28 2.70
 <i>trans</i> 1,4-	i j	1.26 2.70

TABLE 3. RESONANCE ASSIGNMENTS FOR SECONDARY STRUCTURES (^1H NMR)¹⁸

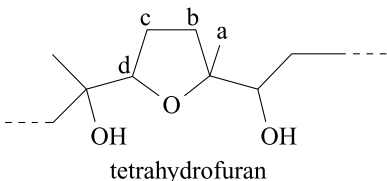
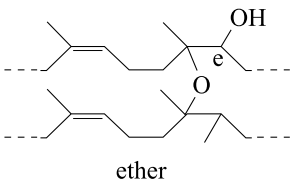
Structures	Protons	Chemical shifts (p.p.m.)
 tetrahydrofuran	a b, c d	1.15 1.8 3.9
 ether	e	3.4

TABLE 4. IR CHARACTERISATION OF 1,4-POLYISOPRENES CONTAINED IN THE LATICES

Vibration	$\nu_{=\text{CH}}$	$\nu_{\text{C-H}}$	$\nu_{\text{C=C}}$	$\nu_{\text{C-H}}$	$\nu_{=\text{CH}}$
Position (cm^{-1})	3035	2961–2728	1665	1451–1378	837

TABLE 5. IR CHARACTERISATION OF EPOXIDISED 1,4-POLYISOPRENES OBTAINED AFTER EPOXIDATION OF THE VARIOUS LATICES

Vibration	ν_{CO} (Symmetrical)	ν_{CO} (Asymmetrical)	ν_{OH} (Ring-opened)	ν_{CO} (Tetrahydrofuran)	$\nu_{\text{C=O}}$
Position (cm^{-1})	1255	889	3500	1060	1720

by considering the respective influences of nature and concentration of the surfactant used to improve the latex stability, the reaction temperature, the formic acid and hydrogen peroxide concentrations. To study the effect of the various parameters, each was varied keeping the others constant. During the entire study, partial epoxidation conditions were examined (a 30% theoretical epoxidised unit content related to hydrogen peroxide was chosen to study the influence of surfactant and of temperature: $r_t = (\text{H}_2\text{O}_2)/(\text{polyisoprene units}) = 0.3$, and the latices were brought to 20% DRC.

Effect of the Surfactant

Without stabilisation by a surfactant, the epoxidation of NR latex at 60°C is not possible because of the spontaneous latex coagulation on the addition of the formic acid. However, the epoxidation of LIR-700 latex performed under the same conditions did give good results as shown in *Figure 2*. After 48 h, the epoxidised unit content is about 84%.

These results can be easily explained by the proper characteristics of the respective latices. The dispersion of rubber particles in the latex is due to their charges and their solvation, and latex stability depends on pH. The pH of the freshly collected field latex is between 6.5 and 7.5, and the isoelectric point which corresponds to the neutralisation of the charges is noted at $\text{pH} = 4.7$. So, the neutralisation

of the particle charges by addition of acid (by varying the pH) (*Figure 3*) or the protein coating destruction (for instance, by addition of alcohol), would lead automatically to latex coagulation. Consequently, it is clear that formic acid is responsible of the NR latex coagulation, because it always occurs at $\text{pH} = 4.7$ at any temperature (30°C, 40°C, or 60°C). In the case of LIR-700 latex, the absence of coagulation observed after addition of formic acid, and therefore the success of the epoxidation reaction (*Figure 2*), is due to the very low pH of this synthetic latex ($\text{pH} = 2$ at 60°C). This stability at low pH is in part contributed by the polyoxyethylene type non-ionic surfactants.

The coagulation of NR latex can be suppressed by incorporating surfactants as shown in *Figures 3* and *4*. For any surfactant used (cationic, anionic, amphotere, non-ionic), a large increase of its stability is noted (*Figure 4*). At 60°C, the pH of NR latex (DRC 20%) is equal to 8.3. After addition of 3 p.h.r. of anionic (SDS) or non-ionic surfactant (Sinnopal NP 307[®]) no destabilisation is observed, even at very low pH (*Figure 4*). On the other hand, when the anionic (or non-ionic) surfactant is replaced with 3 p.h.r. of a cationic (Norianum MC 50[®]) or an amphotere (*N,N*-dimethyl lauryl betaine) surfactant, the coagulation occurs but at a pH lower than that corresponding to the coagulation of the crude NR latex (0.8 and 1, respectively).

At 60°C, the pH of LIR-700 latex (DRC 20%) is equal to 1.4. Like NR latex, it remains

stable at a very low pH when it is stabilised with 3 p.h.r. of SDS or Sinnopal NP 307® (*Figure 5*). However, when its stabilisation is achieved with 3 p.h.r. of Noranium MC 50® or *N,N*-dimethyl lauryl betaine (LNB), destabilisation is noted at pH about 0.3 (irreversible coagulation with the cationic surfactant, reversible demixion with the amphotere one) (*Figure 5*).

Epoxidation does not occur with latices stabilised with the anionic surfactant (3 p.h.r. of SDS), whatever the latex used (NR or LIR-700), the latices remain perfectly stable. The reactions were performed at 60°C with equimolar quantities of formic acid and hydrogen peroxide, and the latex pH after addition of the totality of the reagents was 2.7 for NR latex and 1.5 for LIR-700.

Contrary to the reaction performed with latices stabilised with anionic surfactants, epoxidation of the latices stabilised with 3 p.h.r. of a cationic surfactant (Noranium MC 50®) is possible. The epoxidations were performed at different temperatures (30°C, 40°C, and 60°C), with equimolar quantities of formic acid and hydrogen peroxide. The results summarised in *Table 6*, show that the epoxidation yield obtained was very low, which can be explained by the ability of the latices to destabilise during epoxidation. Moreover, they were all lower as the reaction temperature was high. This surprising result is explained by the fact that latex coagulation that occurs while the epoxidation is in progress, is favoured by the increase of temperature. To avoid latex destabilisation, the reaction must be carried out at low temperatures (at 30°C for instance, as shown in *Table 6*) which require increased reaction time to obtain reasonable epoxidised unit content.

Results similar to those obtained with latices stabilised with the cationic surfactant, were observed with the amphotere surfactant. By replacing SDS by *N,N*-dimethyl lauryl betaine

(3 p.h.r.), latex coagulation also occurs during the epoxidation progress when the reaction is carried out under the same conditions, that is 60°C with equimolar quantities of formic acid and hydrogen peroxide, and $r_i = 0.3$ (complete coagulation after 9 h of reaction with NR latex, against 24 h with LIR-700 latex). However, at same time, epoxidation is much faster than with latices stabilised with SDS (*Figure 6*).

The best results were obtained with latices stabilised with non-ionic surfactants. In the presence of 3 p.h.r. of a non-ionic surfactant, the latices become less sensitive to pH variations and their stability is highly improved²⁴. Partial epoxidations (theoretical epoxidised unit content = 30%) of NR and LIR-700 latices stabilised with 3 p.h.r. of various non-ionic surfactants (*Table 7*) were performed at 60°C with equimolar quantities of formic acid and hydrogen peroxide. Whatever the surfactant used, the kinetic curves obtained were very close (*Figure 7*). However, the final values of epoxidation yield depend on the structure of the surfactant used. The best epoxidised unit content, as well as the best reaction kinetics, were always obtained with latices stabilised with Sinnopal NP 307® (polyoxyethylene α -nonylphenyl ether), whatever the initial latex (NR or LIR-700). At the end of the reaction, that is 78 h, it was noted that the epoxidised latices coming from LIR-700 latex were perfectly stable, which was not the case of those coming from NR latex. With most of the surfactants used to improve the stability of NR latex during its epoxidation, coagulation of the rubber was observed during reaction, except when Sinnopal NP 307® and Brij 35® were used.

These results led us to select Sinnopal NP 307® as the surfactant able to stabilise the rubber latices for the following studies.

In summary, whatever the nature of the surfactant added to NR latex, the stability

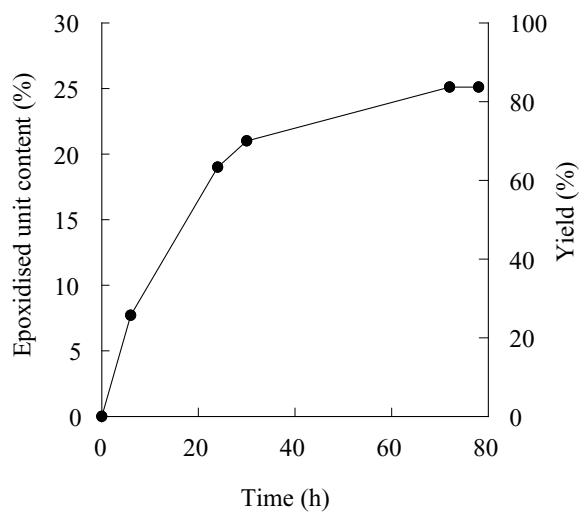


Figure 2. Progress of epoxidised unit content of LIR-700 latex without addition of any surfactant, 60°C, $r_i = (H_2O_2)/(Polyisoprene\ units) = 0.3$, $r = [HC(O)OH]/(H_2O_2) = 1$.

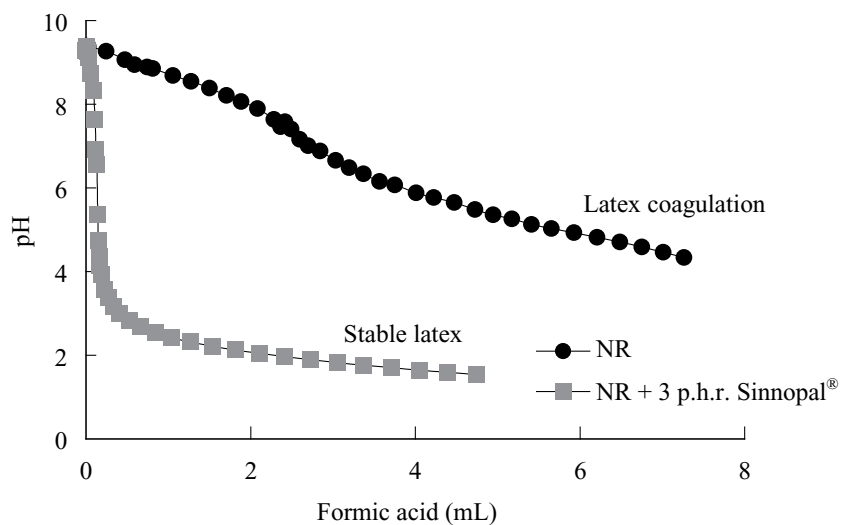


Figure 3. Control of the stability of NR latex (DRC 20%) according to pH, 30°C.

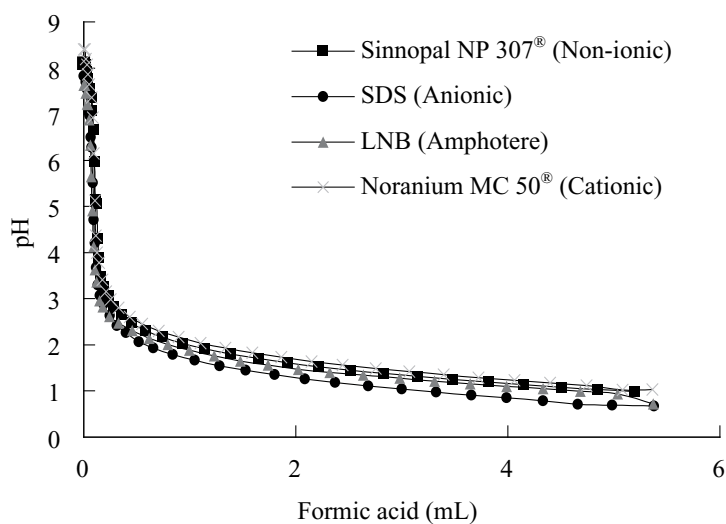


Figure 4. Control of the stability of NR latex (DRC 20%) according to surfactant nature and pH. Studies performed at 60°C with 3 p.h.r. of the following surfactants: Sinnopal NP 307[®], SDS, N,N-dimethyl lauryl betaine (LNB), and Noranium MC 50[®].

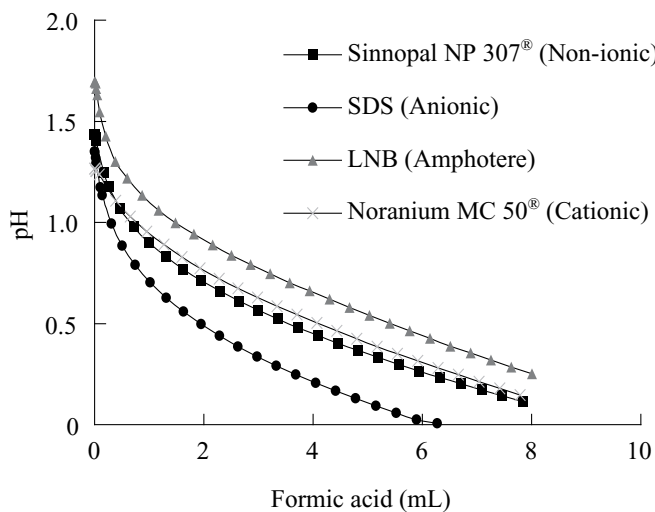


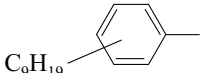
Figure 5. Control of the stability of LIR-700 latex (DRC 20%) according to surfactant nature and pH. Studies performed at 60°C with 3 p.h.r. of the following surfactants: Sinnopal NP 307[®], SDS, N,N-dimethyl lauryl betaine (LNB), and Noranium MC 50[®].

TABLE 6. STUDY OF THE EPOXIDATION OF LATICES
(THEORETICAL EPOXIDISED UNIT CONTENT = 30%) STABILIZED WITH A CATIONIC
SURFACTANT (3 p.h.r.), 60°C, 24 H, $r = [\text{HC}(\text{O})\text{OH}]/(\text{H}_2\text{O}_2) = 1$

Temperature	Natural Rubber Latex			Synthetic Polyisoprene Latex (LIR-700)		
	Epoxidised unit content (%)	Yield ^a (%)	Remark	Epoxidised unit content (%)	Yield ^a (%)	Remark
30°C	7	23	Latex stable after 24 h	3.6	12	Latex stable after 24 h
40°C	4	13	Coagulation after 2 h	5.3	18	Demixion after 6 h
60°C	0	0	Coagulation after 15 min	1.8	6	Demixion after 2 h

^aRelated to the initial content in epoxidised unit.

TABLE 7. STRUCTURES OF THE VARIOUS NON-IONIC SURFACTANTS
USED: $\text{R}-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{OH}$ ($\text{R} = \text{n-ALKYL}$)

Surfactant	Name	R	n
Sinnopal NP 307 [®]	Polyoxyethylene α -nonylphenyl ether	C_9H_{19} 	30
Brij 98 [®]	Polyoxyethylene (20) oleyl ether	$\text{C}_{17}\text{H}_{35}$	20
Brij 30 [®]	Polyoxyethylene (4) lauryl ether	$\text{C}_{12}\text{H}_{25}$	4
	Polyoxyethylene (10) tridecyl ether	$\text{C}_{13}\text{H}_{27}$	10
Brij 56 [®]	Polyoxyethylene (10) cetyl ether	$\text{C}_{16}\text{H}_{33}$	10
Brij 96 [®]	Polyoxyethylene (10) oleyl ether	$\text{C}_{17}\text{H}_{35}$	10
Brij 35 [®]	Polyoxyethylene (23) lauryl ether	$\text{C}_{12}\text{H}_{25}$	23
Brij 58 [®]	Polyoxyethylene (20) cetyl ether	$\text{C}_{16}\text{H}_{33}$	20

of the latter was always improved (even when it was brought to low pH), even if this improvement is less significant with the cationic and amphotere surfactants which avoid the coagulation at the condition to maintain the latex at $\text{pH} > 1$. Consequently, the reinforcement of the stability of NR latex was the result of an equilibrated repartitioning of the electrophilic and electrophobic parts of the

surfactant at the interface between the rubber particles and the aqueous medium. Without surfactant, NR latex systematically coagulates at $\text{pH} 4.7$; the pH which corresponds to the neutralisation of the totality of the charges of the stabilising protein layer present at the surface of rubber particles, and thus to the suppression of the repulsive forces which make it possible to preserve the stability of

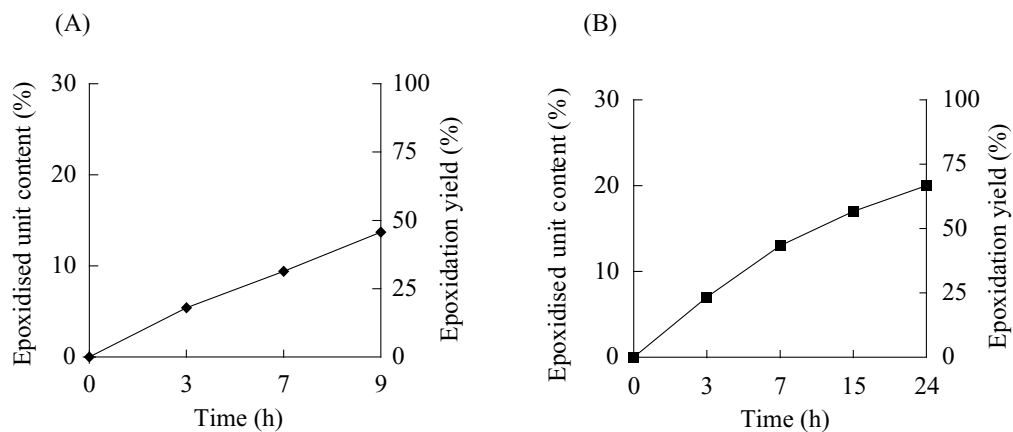


Figure 6. Progress of epoxidised unit content of NR latex (A) and LIR-700 latex (B) stabilised with 3 p.h.r. of N,N-dimethyl lauryl betaine, 60°C, $r_t = (\text{H}_2\text{O}_2)/(\text{polyisoprene units}) = 0.3$, $r = [\text{HC(O)OH}]/(\text{H}_2\text{O}_2) = 1$.

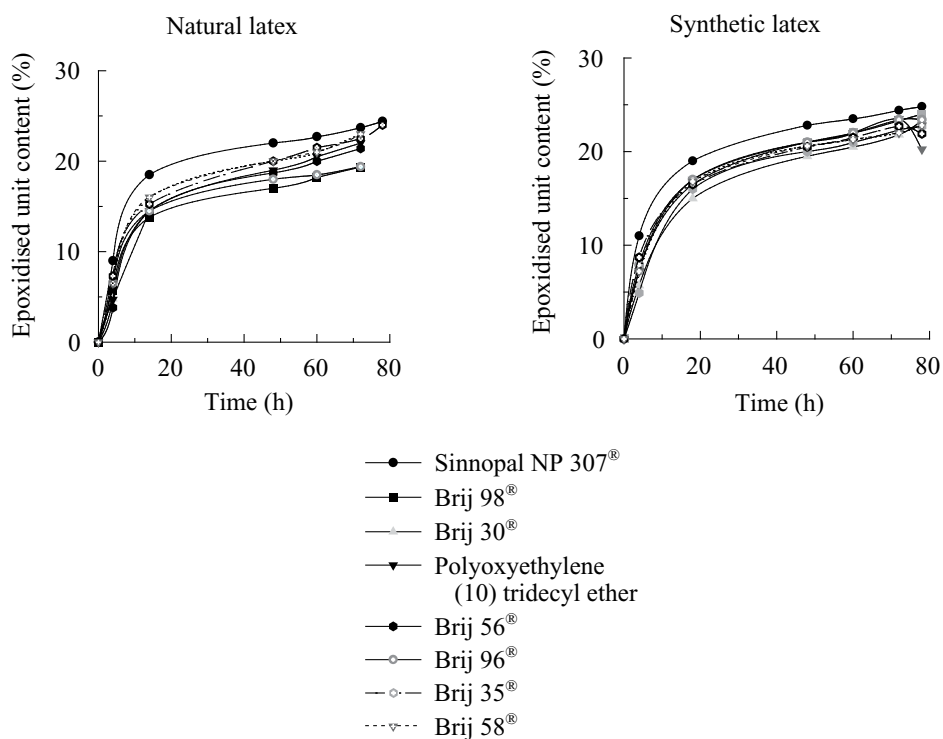


Figure 7. Study of the epoxidation progress of NR and LIR-700 latices (theoretical epoxidised unit content = 30%), according to the non-ionic surfactant (3 p.h.r.), 60°C, $r_t = (\text{H}_2\text{O}_2)/(\text{polyisoprene units}) = 0.3$, $r = [\text{HC(O)OH}]/(\text{H}_2\text{O}_2) = 1$.

the latex. At this moment, aggregation of the rubber particles could occur leading to coagulation of the latex. On the other hand, the absence of epoxidation when the reaction was performed with NR latex stabilised with an anionic surfactant was more difficult to explain. However, it could be assumed that the negative charges at the surface of the particles, brought by the anionic surfactant, could induce repulsive effects towards the performic acid reagent and thus, prevent its penetration inside the rubber particle.

Effect of Temperature

Consequent to the results related above, the influence of temperature was studied with LIR-700 and NR latices previously stabilised with 3 p.h.r. of Sinnopal NP 307[®]. Moderate temperatures of 40°C, 60°C and 70°C respectively, were selected to avoid the coagulation of the latices, and the epoxidations were carried out with equimolar quantities of hydrogen peroxide and formic acid calculated to obtain a theoretical epoxidised unit content of 30%.

The results summarised in *Figure 8* showed that LIR-700 and NR latices had similar behaviours. Their epoxidation rates according to reaction temperature were in good accordance: in two cases, the epoxidation rates greatly increased when the reaction temperature was increased, but too high a temperature (higher than 70°C) caused coagulation of latex. The epoxidation of the respective latices was totally selective when the epoxidation was performed at 40°C or 60°C. On the other hand, this selectivity disappeared when the temperature reaction was brought to 70°C: for each of the latices, a maximum value of the epoxidation rate was noted after 40 h – 50 h of reaction. The decrease of epoxidation rate observed was explained by the opening of part of the oxirane rings because of the medium acidity. The presence of tetrahydrofuran rings on the epoxidised polyisoprene chains coming from

LIR-700 latex were characterised by ¹H NMR ($\delta = 3.9$ p.p.m.). Vibrations characteristic of α,β -diol structures were also noticed on the IR spectra ($\nu_{\text{OH}} = 3500 \text{ cm}^{-1}$). The effects of secondary reaction were less important with NR latex. The global proportion of secondary units formed after 78 h of reaction was estimated to about 3% of the epoxidised units formed with LIR-700 latex, while in the case of NR latex it was too low to be measured.

As at 70°C, the prolongation of reaction time favours the opening of the oxirane rings, 60°C was considered as a convenient temperature. Indeed, at this temperature, the secondary reactions did not occur and the epoxidation rate was relatively fast.

Effect of Surfactant Concentration

To verify the influence of surfactant concentration on the epoxidation progress, various concentrations of Sinnopal NP 307[®] were considered. Epoxidations of NR and LIR-700 latices stabilised with 2 p.h.r., 3 p.h.r., 5 p.h.r., 8 p.h.r., and 12 p.h.r. respectively, were carried out at 60°C with equimolar quantities of formic acid and hydrogen peroxide calculated to obtain a theoretical epoxidised unit content of 30%. The progressions of the various epoxidations performed with the two latices are given in *Figure 9*. It was noted that, at same concentration of Sinnopal NP 307[®], the epoxidation rates observed with the two latices were similar. Moreover, in the case of NR latex, and in a less obvious way with LIR-700, the rates of epoxidation were the same when the surfactant concentration used was below 5 p.h.r. With higher concentrations, it was noted that the higher the Sinnopal NP 307[®] concentration, the slower the epoxidation rate. Finally, at the end of the reaction, the epoxidised unit contents were always the same whatever the Sinnopal NP 307[®] concentration used, and secondary processes did not occur. Kinetic slowdown was observed when Sinnopal

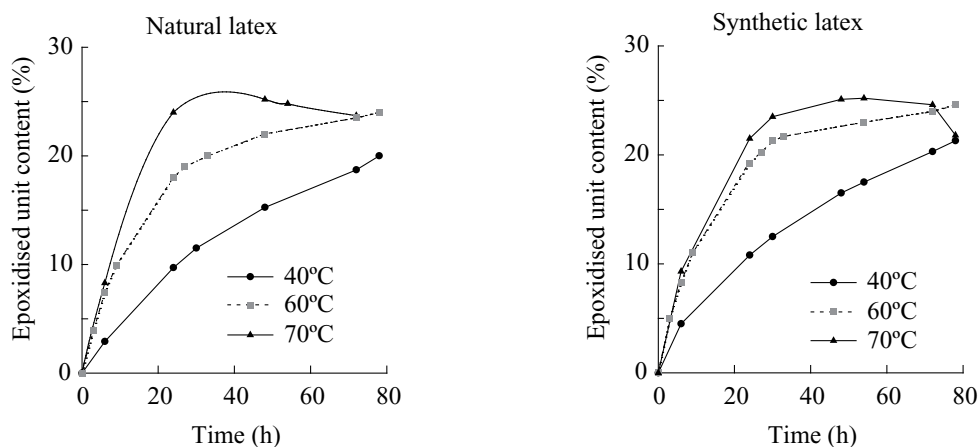


Figure 8. Study of the epoxidation progress of NR and LIR-700 latices (theoretical epoxidised unit content = 30%), according to temperature. Sinnopal NP 307[®] (3 p.h.r.), $r_t = (H_2O_2)/(\text{polyisoprene units}) = 0.3$, $r = [HC(O)OH]/(H_2O_2) = 1$.

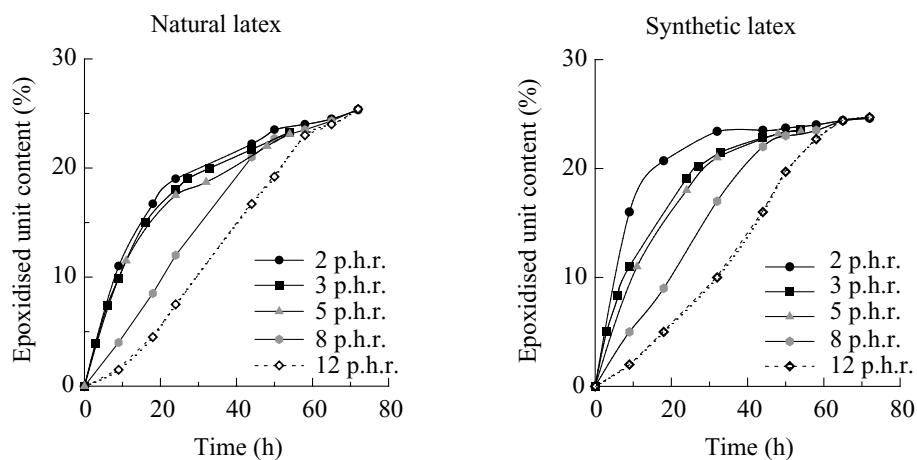


Figure 9. Study of the epoxidation progress of NR and LIR-700 latices (theoretical epoxidised unit content = 30%), according to Sinnopal NP 307[®] concentration, 60°C, $r_t = (H_2O_2)/(\text{polyisoprene units}) = 0.3$, $r = [HC(O)OH]/(H_2O_2) = 1$.

NP 307[®] concentration was decreased below 5 p.h.r., this can be interpreted in terms of thickness of the interfacial barrier which must necessarily be crossed by the peracid. These results confirm the position of the surfactant at the interface rubber particles / dispersing medium. The use of Sinnopal NP 307[®] concentrations near 3 p.h.r. to stabilise NR or LIR-700 latices seemed a convenient choice.

Effect of Acid Concentration

To study the influence of formic acid concentration on the progress of the epoxidation of NR and LIR-700 latices, several molar ratios $r = (\text{formic acid})/(\text{hydrogen peroxide})$ (0.5, 1, 2, and 3) were considered while keeping hydrogen peroxide concentration constant ($r_1 = 0.3$). The epoxidation were performed at 60°C with both latices previously stabilised with 3 p.h.r. of Sinnopal NP 307[®].

The results summarised in *Figure 10* show that NR and LIR-700 latices react similarly. When formic acid concentration was increased, the epoxidation rate accelerated, but on the other hand the effects of secondary reactions were favoured. These were observed when $r = 3$, as shown by the decrease of epoxidation yield observed after 48 h of reaction (with NR latex) or 18 h (with LIR-700 latex). The analysis of the epoxidised rubbers by ¹H NMR spectroscopy showed that there was formation of furan cycles and α,β -diol groups (and/or ether interchain bonds), their proportions after 78 h of reaction was about 2% of the theoretical content of epoxidised units in the case of NR latex and 3% for LIR-700 latex.

The formation of secondary units was noted when $r > 1$. However, in comparison with the epoxidation reaction, the kinetics of formation of secondary units derived from epoxidised ones were much slower, which explains why they were characterised only when the epoxidation reaction was almost

complete. On the other hand, when $r \leq 1$, they were totally absent: after 78 h of reaction, no signal characteristic of secondary units was noted on the ¹H NMR or Infrared spectra of the epoxidised rubbers obtained.

It arises that the best selectivity of epoxidation was observed when equimolar quantities of formic acid and hydrogen peroxide were used. However, excess of formic acid compared with hydrogen peroxide could be used, but at the condition to stop the reaction before the appearance of the secondary structures. In addition, the results obtained here also show that the level of epoxidised units in the epoxidised latex was monitored by the concentration of hydrogen peroxide: it depended directly on the value of r_1 .

Effect of Peroxide Concentration

The effect of hydrogen peroxide concentration was studied at 60°C by varying the molar ratio $r_1 = (\text{H}_2\text{O}_2)/(\text{Polyisoprene units})$, that is the theoretical epoxidised content as shown above. At the same time, $[\text{HC(O)OH}]/(\text{Polyisoprene units})$ was maintained as equal to 0.3. The experiments were performed with NR and LIR-700 latices previously stabilised with 3 p.h.r. of Sinnopal NP 307[®].

The progress of epoxidations carried out with excess or default of hydrogen peroxide compared with formic acid were related to that of epoxidation performed when hydrogen peroxide and formic acid were used in equimolar quantities (*Figure 11*). A good concordance was observed between the progress of epoxidation of NR latex and that of LIR-700 latex when the reaction was performed under the same conditions. It was also noted that the epoxidised contents obtained at the end of the reaction, as well with NR latex as LIR-700 latex, increased when the concentration of hydrogen peroxide was increased. This was confirmation that the

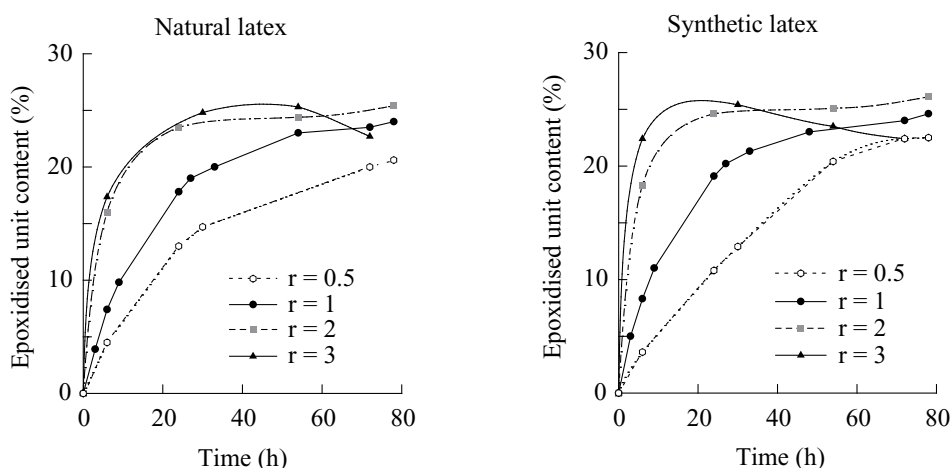


Figure 10. Study of the epoxidation progress of NR and LIR-700 latices, according to formic acid concentration (variation of $r = [\text{HC}(\text{O})\text{OH}]/(\text{H}_2\text{O}_2)$, Sinnopal NP 307[®] (3 p.h.r.), 60°C, $(\text{H}_2\text{O}_2)/(\text{polyisoprene units}) = 0.3$.

TABLE 8. EPOXIDATION YIELDS OBTAINED AFTER 168 H FOR VARIOUS THEORETICAL EPOXIDISED UNIT CONTENTS WHEN $[\text{HC}(\text{O})\text{OH}]/(\text{POLYISOPRENE UNITS}) = 0.3$

Theoretical epoxidised unit content	Epoxidation yield with NR latex	Epoxidation yield with LIR-700 latex
60% ($r_t = 0.6$)	82%	75%
30% ($r_t = 0.3$)	81%	82%
25% ($r_t = 0.25$)	80%	83%
20% ($r_t = 0.20$)	80%	83%
15% ($r_t = 0.15$)	77%	79%
10% ($r_t = 0.10$)	57%	57%
7% ($r_t = 0.07$)	43%	51%

polyisoprene epoxidation level was close to the hydrogen peroxide concentration.

In addition, it was also noted that the epoxidation yield depended on the hydrogen peroxide concentration (Table 8). When hydrogen peroxide concentration was calculated to epoxidise more than 15% of the polyisoprene units, the yield obtained after 168 h were almost same (about 80%). On the other hand,

below this 15% limit value, a decrease of the epoxidation yield was noted. This yield decrease was all the higher as the hydrogen peroxide was low. The effects of secondary reactions could explain this yield decrease, but unfortunately it was also noted that these secondary reactions were favoured when the hydrogen peroxide concentration r_t was increased. For instance, the secondary unit content after 78 h of reaction performed with $r_t = 0.6$ represented about 3% of

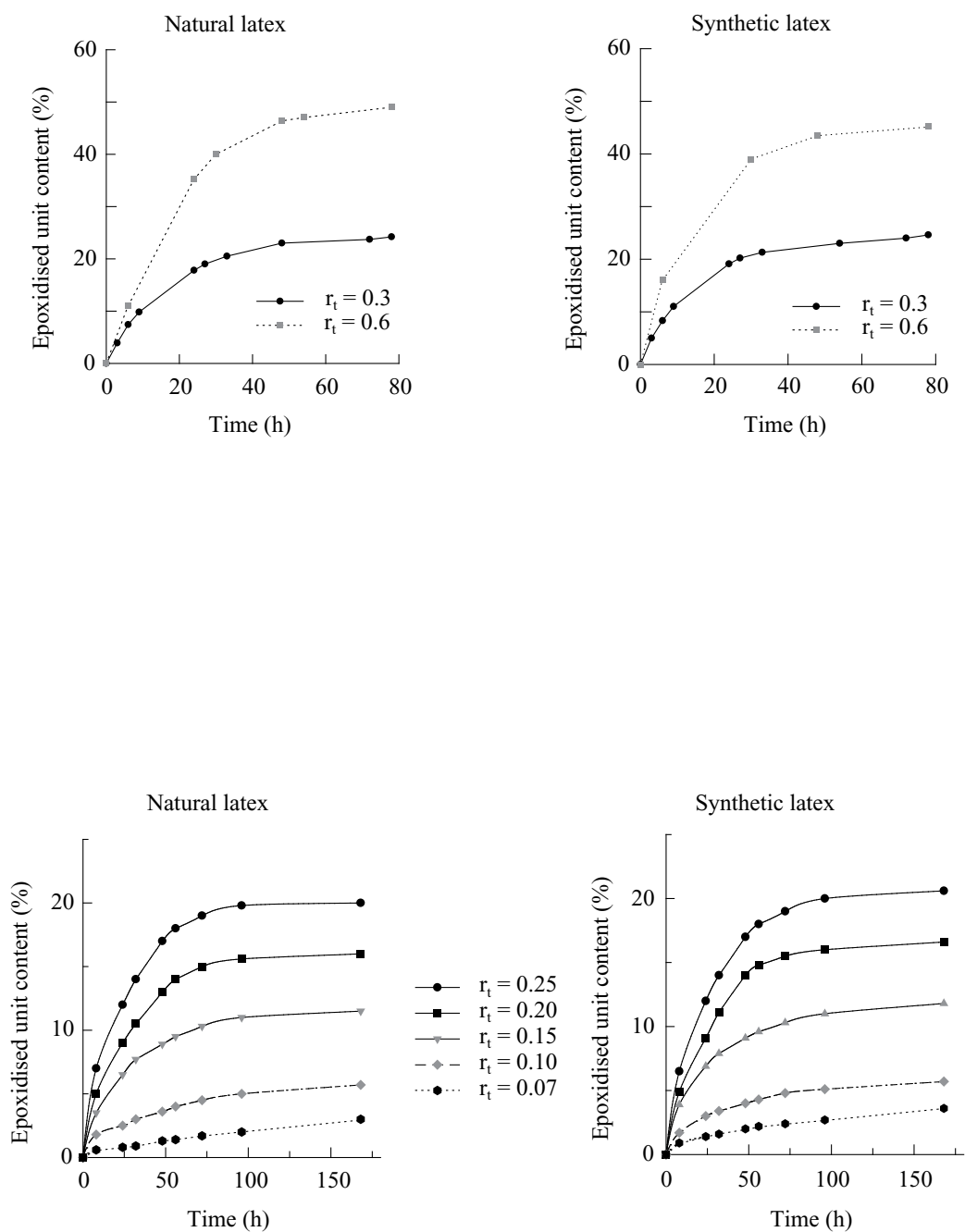


Figure 11. Study of the epoxidation progress of NR and LIR-700 latexes, according to hydrogen peroxide concentration (variation of $r_t = (\text{H}_2\text{O}_2)/(\text{polyisoprene units})$, Sinnopal NP 307® (3 p.h.r.), 60°C, $[\text{HC}(\text{O})\text{OH}]/(\text{polyisoprene units}) = 0.3$.

the initial epoxidised units for NR latex against 4% for LIR-700 one, while no secondary unit was observed when $r_t = 0.3$. On the other hand, the explanation could be given by taking into account the progress of reaction rate. As the epoxidation rate was all the slower as r_t was low, one can consider that the epoxidation reaction was probably influenced by the polarity of the rubber chains: the reaction of performic acid, and so its penetration in the rubber particles, would be all the easier as the epoxidised unit content in the rubber would be high.

Stability of the Epoxidised Latices

The destabilisation of the various epoxidised latices were followed by turbidimetry using the Turbiscan MA 1000. It was characterised by a retro-diffusion decrease in the lower part of the tube and a retro-diffusion increase at the top part of the tube (*Figure 12*).

The progress with time, of latex creaming of the epoxidised latices coming from NR and LIR-700 latices are shown in *Figures 13* and *14*, respectively, as well as that of the starting latices characterised before and after stabilisation with 3 p.h.r. of Sinnopal NP 307®. As in the case of the non-modified rubber latices, the epoxidised latex derivatives show a creaming phenomenon associated to particle aggregation. Whatever the starting latex (NR or LIR-700), it was normally observed that their stability was improved after addition of 3 p.h.r. of Sinnopal NP 307®. Concerning the stability of the resulting epoxidised latices, the results surprisingly depend on the nature of the starting latex used: the stability of ELIR was better compared with that of LIR-700 even when stabilised with Sinnopal NP 307®, whereas that of ENR appears intermediate between that of the crude NR latex and that of LIR-700 stabilised with 3 p.h.r. Sinnopal NP 307®.

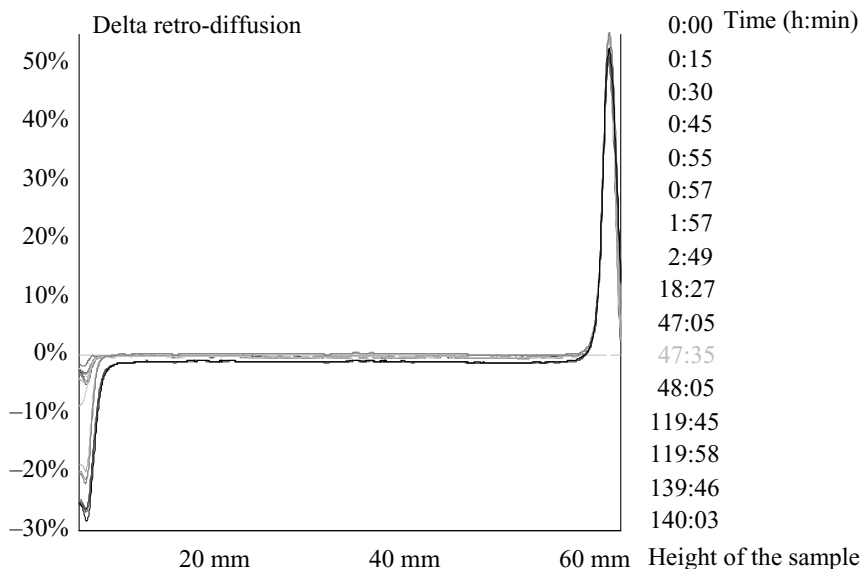


Figure 12. Destabilisation of 20% ENR latex resulting from epoxidation of NR latex (DRC 20%).

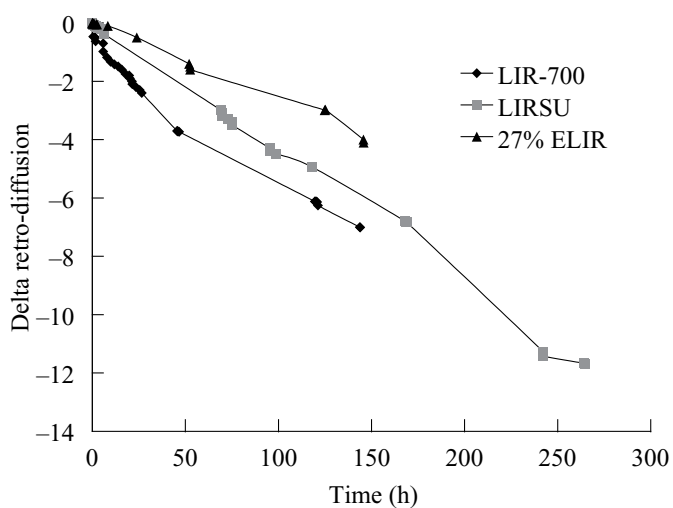


Figure 13. Creaming rates of the various latices derived from LIR-700 latex: Initial synthetic polyisoprene latex (LIR-700), LIR-700 stabilised with 3 p.h.r. of Sinnopal NP 307[®] (LIRSU), 27% epoxidised LIR-700 latex (27% ELIR); measures performed on the bottom of the tube containing the sample (between 6.2 mm and 9.2 mm).

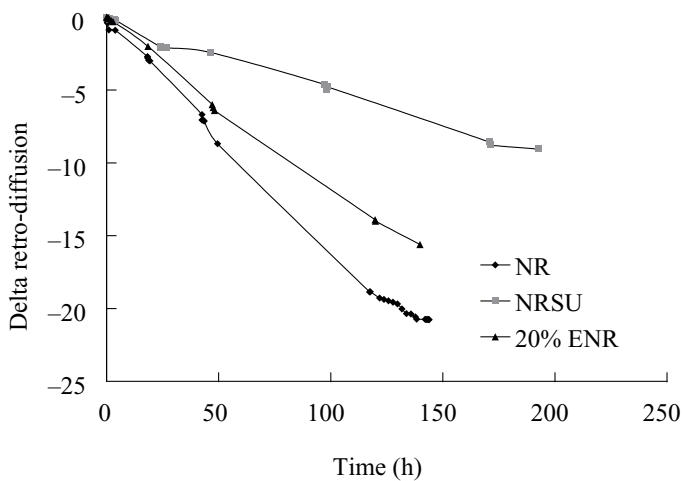


Figure 14. Creaming rates of the various latices derived from NR latex: initial natural rubber latex (NR), NR latex stabilised with 3 p.h.r. of Sinnopal NP 307[®] (NRSU), 20% epoxidised NR latex (20% ENR); measures performed on the bottom of the tube containing the sample (between 6.4 mm and 10 mm).

CONCLUSIONS

Systematic studies of epoxidation were performed on a synthetic polyisoprene latex (LIR-700) and a NR latex with performic acid generated *in situ* from the couple hydrogen peroxide/formic acid, and the respective results obtained according to the various parameters of the reaction (nature and concentration of surfactant used, reaction temperature, and quantities of formic acid and hydrogen peroxide used to form performic acid) were compared. On the whole, at similar epoxidation conditions, the results obtained with LIR-700 and NR latices were shown to be very close. The only marked difference was noted when the reaction was carried out on the crude latices, that is before addition of surfactants to improve their stability: it was noted that epoxidation took place with LIR-700 latex which already contains surfactants able to authorise the epoxidation, while it cannot occur with NR latex which immediately coagulates when formic acid is added. Consequently, LIR-700 can be considered as a good model of NR latex to develop new chemical reactions in latex medium before their generalisation to NR latex whose composition is very complex due to the presence of non-rubber compounds.

The purpose was also to define the optimised epoxidation conditions leading to stable epoxidised polyisoprene latices and ensuring selective epoxidation, that is without secondary processes. For that, the epoxidation must be carried out on latices previously stabilised with 3 p.h.r. of a non-ionic surfactant (Sinnopal NP 307® for example), at a temperature of 60°C and with equimolar quantities of formic acid and hydrogen peroxide.

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