ON THE STABILITY OF NATURAL RUBBER LATEX ACIDIFIED BY ACETIC ACID AND SUBSEQUENT EPOXIDATION BY PERACETIC ACID

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Abstract—Natural rubber (NR) latex having up to 54% dry rubber content (drc), stabilized by 1.65–5.0 parts of nonionic surfactant [(fatty alcohol)/(ethylene oxide) condensate type] per hundred of rubber can be acidified by acetic acid to pH *ca* 4, retaining good aggregative stability. It was shown that this stability depends on drc, surfactant level and final pH. The stabilized latex of medium-to-high drc (25–48%) could be successfully subjected to epoxidation at moderate temperature, using preformed peracetic acid. The epoxidation proceeds rapidly and effectively, leading to pure ENR of up to 60–70 mol% epoxide content as checked by i.r. and ¹H-NMR. By swelling test and sol-gel fractionation, it was shown that the epoxidation reduces the solubility of rubber in nonpolar solvents and increases its sensitivity to polar solvents. The long lasting and highly acidic medium of reaction lead to increase in the gel content of ENR samples compared with the original NR.

INTRODUCTION

Among many possibilities of chemical modification of natural rubber (NR), epoxidation is a simple and efficient method to introduce a new reactive group onto the polyisoprene backbone, leading to new and useful properties [1, 2]. Although it was tried over 60 years ago [3], only in the last decade has this reaction been carried out successfully in latex, using preformed peracid [4]. Up to now, there has been only one paper studying the epoxidation of NR acidified by acetic acid [5] but the reaction was performed using relatively dilute latex [*ca* 15% dry rubber content (drc)] at low temperature (0–5°).

Continuing our studies on the stability and epoxidation of NR in latex stabilized by nonionic surfactants in the presence of acidic agents (such as HCl [6] or formic acid [7]) as well as on the stability of the epoxidized products [8], we now present results on a latex system acidified by acetic acid. The paper will deal in detail with the aggregative stability of NR latex stabilized by additional nonionic surfactant of the (fatty alcohol)/(ethylene oxide) condensate class in the presence of acetic acid.

The epoxidation of NR by peracetic acid, using latex of medium-to-high dry rubber contents, will be investigated. The product of the reaction after isolation and purification was characterized and studied by various methods and techniques (chemical and spectral analysis, DSC, swelling test and sol-gel determination).

EXPERIMENTAL PROCEDURES

Materials

1. NR latex: Centrifuged, full ammonia latex of 57.7% drc (Qualitex).

2. Surfactant: nonionic, (fatty alcohol)/(ethylene oxide) condensate: Verol S-15 (Verila, Bulgaria), product having cloud point of 72–75°.
3. Glacial acetic acid, p.a (Fluka).
4. Hydrogen peroxide, 30% aqueous, purum (Fluka).
5. Acetic anhydride, p.a (Fluka).
All other materials (reagent grade) were used as supplied.

Procedure

Synthese of peracetic acid. Peracetic acid can be synthesized from acetic acid or acetic anhydride and hydrogen peroxide at moderate temperature (35–40°) [9]. The synthesis from acetic anhydride needs no catalyst and is more convenient. From 30% aq. H₂O₂ and acetic anhydride, peracetic acid of 20 ± 2% by weight can be obtained. The peracid is not stable at room temperature and must be stored at *ca* −10°. In the peracetic acid, 6–7% H₂O₂ remains.

Acidification. The process of acidification has been described [6, 7]. The NR latex was stabilized by adding with continuous stirring the necessary amount of nonionic surfactant (as 20% aq. solution) to the initial latex. Acetic acid of known concentration was slowly dropped into this stabilized latex kept with stirring for 30–60 min. The pH was measured by suitable narrow range pH indicator papers. Samples were kept in tightly closed tubes and the time necessary for coagulation at room temperature was noted.

Epoxidation procedure. The reaction was carried out at 25° in a flask equipped with mechanical stirrer, dropping funnel and condenser. The latex stabilized by 1.7–5.0 parts of nonionic surfactant per hundred of dry rubber (phr) was acidified by 50% (w/w) acetic acid to pH of *ca* 5; a determined amount of peracetic acid was dropped in over *ca* 30 min to start the reaction. During the epoxidation, latex samples were

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taken at intervals; the product was isolated by pouring into 50% (v/v) aq. ethanol. The coagulum was washed free of acid and other residues, pressed into a thin sheet (thickness 1–2 mm), soaked for 24 hr at room temperature in 1% Na_2CO_3 solution, washed again to pH = 7 with distilled water and then dried under vacuum at 40° to constant weight before analysis.

Analysis

Peracetic and hydrogen peroxide content was determined by iodometry, using the method of Sully and William [10] (titration with sodium thiosulphate).

Epoxide contents (below than 15–17 mol%): were determined by direct titration with HBr in glacial acetic acid in the presence of crystal violet as indicator (Durbetaki's method [11]). The end point was detected by colour change from violet to blue-green. Higher levels of epoxide content were determined by instrumental methods, viz. i.r. analysis (using the method of Davey [12]), DSC analysis (determination of the glass transition temperature [13]) and ^{1}H-NMR analysis [13].

Sol-gel contents were determined in various solvents at room temperature using a standard method [14]; swelling tests were performed [15].

Apparatus

I.r. spectra were recorded on M-80 spectrograph (Carl-Zeiss, Jena) using film cast directly on KBr plates. ^{1}H-NMR spectra were recorded on Jeol-JNM-PS 100 using solutions in $CDCl_3$. The glass transition temperature was determined as onset value by thermal analysis data station (TADS) using DSC-2C apparatus (Perkin–Elmer).

RESULTS AND DISCUSSION

Investigation on the stability and composition of NR latex in presence of acetic acid

The variations of pH of NR latex on adding acetic acid of various concentrations are shown in Fig. 1. The first four curves refer to the initial latex having 50% drc and stabilized by 1.65 phr of Verol S-15. During the acidification, pH decreases continuously from 9.3 to ca 3.3–4.0 (see Fig. 1, curves 1–4). At high initial drc and relatively low level of additional surfactant, under high acidic concentration (AcOH 50–100%), the acidification can lead to spontaneous coagulation at pH 4 (the moment of coagulation is indicated by a small arrow in Fig. 1, curve 1) or soon after (Fig. 1, curve 2, where coagulation occurred after 2 hr). Systems acidified with acid of lower concentration (<30%) can attain lower pH values without coagulation (pH = 3.3–3.5) and their aggregative stability is much better (Fig. 1, curves 3, 4). These latexes can be stored at pH = 3.5–4 for up to a month before coagulation occurs. Thus, the aggregative stability of NR latex depends greatly not only on the pH but also on the effective drc in the sample. The latex systems having lower drc and higher surfactant levels become more stable and can be acidified to lower pH (pH = 2.8–3.5) without spontaneous coagulation (see Fig. 1, curves 5 and 6 for system of 27% drc and 5 phr Verol S-15). Here, latex of 27% drc treated with glacial acetic acid was stable for 3 days (see also Table 1).

The variation of pH during the acidification of latexes having different drcs and their aggregative stability were also studied. Figure 2 gives the results
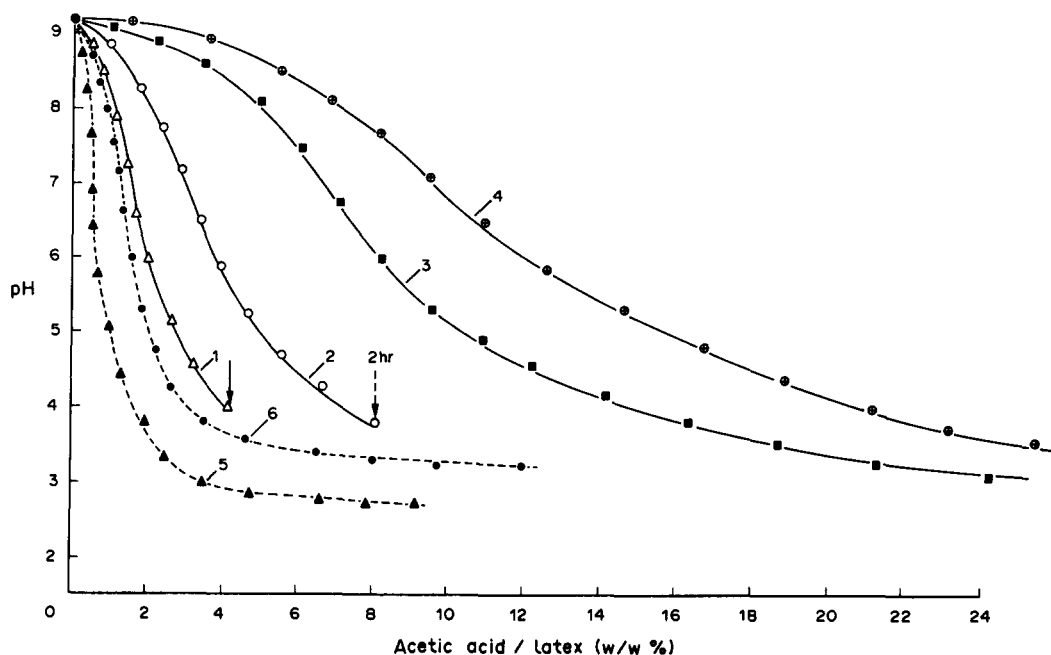

Fig. 1. Variation of pH of NR latex during acidification by acetic acid of various concentrations. Nos 1–4: Latex of 50% drc, stabilized by 1.65 phr Verol S-15, concentrations of acetic acid: 1 (△), glacial acetic acid; 2 (○), 50% AcOH; 3 (■), 30% AcOH; 4 (⊕), 10% AcOH. Nos 5 and 6: Latex of 27% drc, stabilized by 5 phr Verol S-15, concentrations of acetic acid: 5 (▲), glacial acetic acid; 6 (●), 50% AcOH.

Table 1. Stability of NR latex in the presence of acetic acid

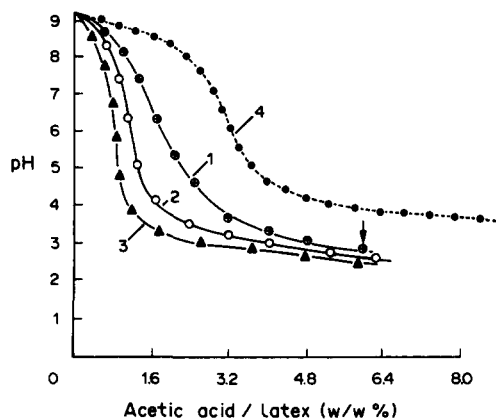| No.	pH regulator	Surfactant	Latex drc	Final pH	Stability
1.	Glac.AcOH	3 phr S-15	52–53	2.9–3.0	Coagulated
2.	50% AcOH	5 phr S-15	53–54	3.0	1 d
3.	Glac.AcOH	5 phr S-15	27	2.9–3.0	3 d
4.	50% AcOH	5 phr S-15	27	3.0	5–6 d
5.	30% AcOH	5 phr S-15	27	3.0	8–10 d

Fig. 2. Variation of pH during acidification of latex with various drc. Nos 1–3: Latexes treated with glacial acetic acid: 1($\oplus$), 54% drc; 2 ($\bigcirc$), 27% drc; 3 ($\blacktriangle$), 12.7% drc. No. 4 ($\bullet$), Latex of 54% drc treated with 30% AcOH.

of acidification by glacial acetic acid of latex systems having 12.7, 27 and 54% drc. Under the influence of high acidic concentration, the pH of latexes changed very quickly and soon reached the limiting range (pH of ca 2.8–3.0). The more dilute latex reached this range sooner (see Fig. 2, compare curves 1, 2 and 3 for latex of 54, 27 and 12.7%, respectively). The latex of higher drc, stabilized by 3 phr of Verol S-15 can be

spontaneously coagulated at pH = 3 (Fig. 2, curve 1) while systems of lower drc are normally much more stable and could be stored for several days at this pH. Figure 2 shows also the variation of pH for 54% drc latex acidified by 30% acetic acid (curve 4). The pH in this case varied less dramatically and the final pH range was higher than for the same latex acidified by glacial acetic acid (compare curves 1 and 4, Fig. 2).

The results on the influence of drc and the final pH on the aggregative stability of latexes are shown in Table 1 for several typical systems. It is seen that the acidification by glacial acetic acid led to spontaneous coagulation or limited aggregative stability. Using more dilute acetic acid for this purpose gave satisfactory stability but could lead easily to excessive dilution of latex (vide infra). According to our experiments, the suitable acidic concentration for acidification of latexes of high drc is 50%.

The variation of the composition of latexes during the acidification was also calculated for several systems, an illustration being presented in Fig. 3. The figure shows the variation in composition of NR latex having initially 54% drc, stabilized by 3 phr Verol S-15 and acidified by 50% acetic acid. During the acidification, the concentration of acid and the water content increased continuously, while the contents of dry rubber and nonionic surfactant gradually decreased. The dilution accompanying the acidification
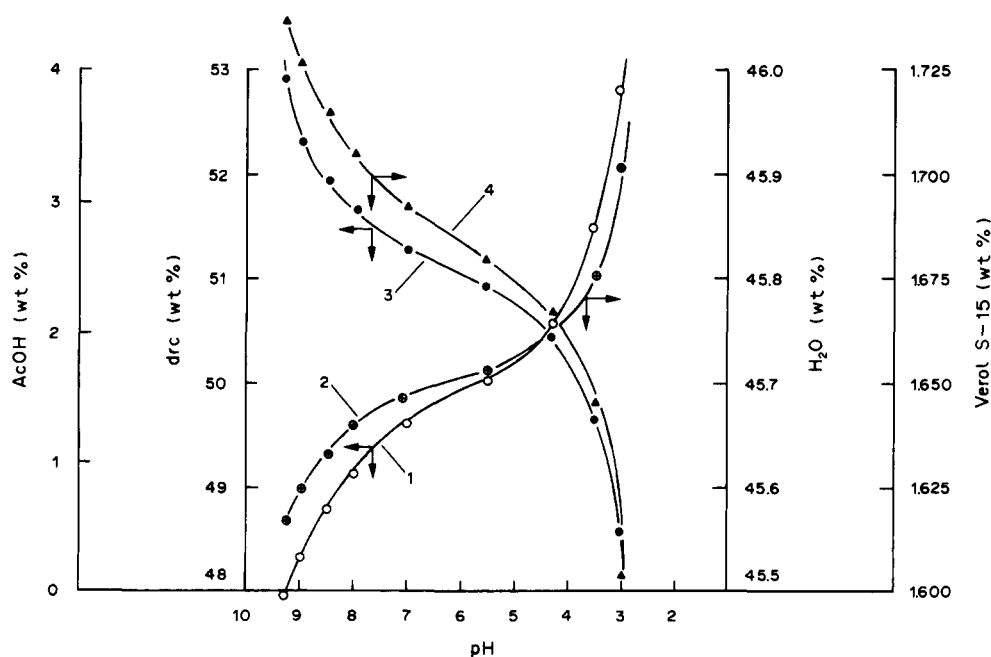

Fig. 3. Variation of composition of NR latex of 54% drc, stabilized by 3 phr Verol S-15 during acidification by 50% AcOH. 1 ($\bigcirc$), AcOH content; 2 ($\oplus$), water content; 3 ($\bullet$), drc; 4 ($\blacktriangle$), surfactant content.

Table 2. Results of epoxidation by peracetic acid

No.	drc (%)	AcOOH/IP M/M	Max epoxide level (Mol%)	Efficiency (%)	T_g (°C)
1.	33.75	0.165	15	91	-54
2.	29.50	0.245	24	98	-47
3.	25.20	0.41	36.5	90	-38
4.	21.00	0.50	47.0	94	-28
5.	18.95	0.70	64.5	92	-13
6.	15.00	1.00	86*	86*	11
7.	12.5	0.21	20	95†	
8.	8.7	0.92	83	90†	

Conditions: Reaction at 25°, initial latex of 48% drc, stabilized by 3.5 phr Verol S-15,
    acidified to pH ca 5.0, using peracetic acid of approx. 22 wt%, $t = 6$ hr with exception
    of No. 6 ($t = 24$ hr).
*Product contaminated by small amount of ring-opened side product as shown by spectral
    methods.
†Data calculated from Ref. [5].

was one of the reasons for the better stability of latexes treated by acetic acid of lower concentration. For acidification by glacial acetic acid, the process led to decrease of all other components while the acidic one was increased and the latex system could be spontaneously coagulated at relatively high pH (see an illustration in Fig. 1, curve 1).

The experiments made with different acidic concentrations, drc and surfactant levels showed that NR latexes having initially 20–50% drc, stabilized by 1.6–5 phr of Verol S-15 are stable at pH at least equal to 4 for days to weeks. The latexes acidified by acetic acid to lower pH show much lower aggregative stability and are not suitable for further transformations under acidic condition. For study of the epoxidation of high drc NR latexes, we conclude that pH of ca 5 offers good stability for both latex and reaction mixture.

Investigation on the epoxidation of NR in latex

As already mentioned, Burfield [5] is the only author who studied the epoxidation of latex acidified by acetic acid using peracetic acid. The reaction was studied under mild conditions (drc of latex subjected to epoxidation was ca 15.5% having 3.3 phr surfactant at 5°). We have studied this reaction at higher drc (25–48%), in the presence of 1.7–5.0% Verol S-15,

using ratios of peracid to isoprene unit from 0.165 to 1.0 M/M, the effective drc in the reaction mixture being 15–34% (see also Table 2).

The reaction was followed by variation of peracetic acid and hydrogen peroxide in the system and the epoxide content of the product. Figure 4 shows typical curves of the variation of peracetic acid and hydrogen peroxide contents during the epoxidation. The end-point of introducing peracid mixture is indicated by an asterisk. It is seen that, during the dropping process, both H_2O_2 and peracetic acid contents continuously increase but the peracid, after reaching a maximum, decreases rapidly because of its fast consumption by direct epoxidation of polyisoprene according to the equation:

$$\text{C=C} + \text{AcOOH} \longrightarrow \text{epoxide} + \text{AcOH}$$
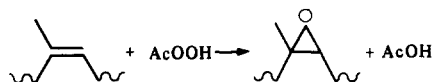
At 25°, the peracetic acid practically disappeared after ca 90 min from the beginning of addition. The hydrogen peroxide, after reaching the plateau, remained practically unchanged during the epoxidation in acidic pH.

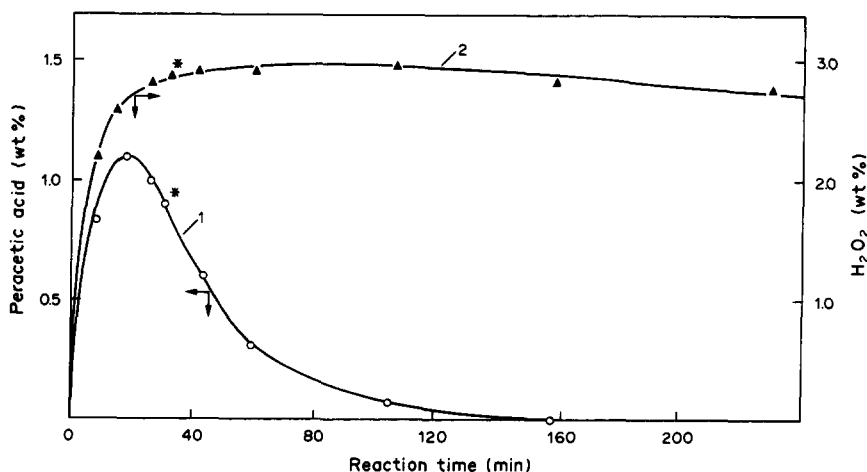These results demonstrate that, at moderate temperature, the epoxidation proceeded quickly enough

Fig. 4. Variation of peracetic acid (1, ○) and hydrogen peroxide (2, ▲) contents during epoxidation at 25°. Reaction conditions: effective drc 23.5%, latex stabilized by 1.75 phr Verol S-15, ratio of peracetic acid/isoprene unit = 0.25 M/M.
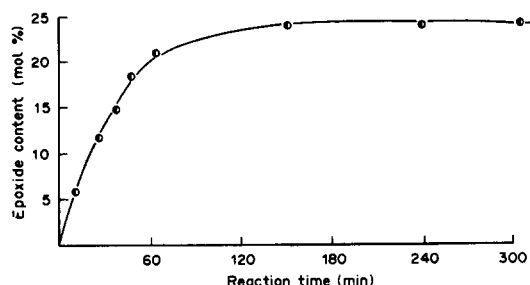
Fig. 5. Variation of epoxide content with reaction time. Reaction conditions: as for Fig. 4.

mostly by consumption of peracetic acid. The hydrogen peroxide present in the reaction system in comparable amount with peracetic acid was hardly involved in the epoxidation.

Variation of epoxide content during the epoxidation is shown in Fig. 5. Formation of epoxide groups started from the beginning of dropping peracetic acid mixture into the latex (compare Figs 4 and 5). The epoxide content increased quickly in the first 30–40 min, then gradually, over ca 90 min, reached ceiling levels very close to the theoretical values. The efficiency of epoxidation, determined as the ratio of mol of epoxide groups to mol of peracetic acid introduced, in particular cases was from 90 to 98% (see Table 2). Even at higher drc, the reaction proceeds normally without spontaneous coagulation, demonstrating the good stability of the latex system.

The moderate conditions of reaction ($t = 25°$, pH = 4.5–5.5 and peracid/isoprene ratio from 0.15 to 0.7) allow control of the epoxidation and lead to pure ENR products (see Table 2 and vide infra). The higher ratio leads partially to ring-opening by-

products accompanying the ENR for systems of initially higher drc (see Table 2). Results of epoxidation of NR in latex acidified by acetic acid are shown in Table 2, together with the corresponding glass transition temperatures determined by DSC for each ENR sample.

Characterization of ENR products

Depending on the epoxide contents, ENR products show a wide range of properties and some i.r. spectral characteristics have already been studied [16]. The products having <50% epoxide groups are elastic, translucent-to-opaque material with off-white colour. ENR of higher epoxide contents become harder, with decreasing elasticity and gradually increasing plasticity. The ring-opening products from ENR of high epoxide contents (80–100 mol%) are white powders, behaving as plastic materials. The glass transition temperature of ENR increased with the epoxide content and can be used to determine the epoxidation level as proposed by others [11, 12] (see also Table 2).

Figure 6 shows typical i.r. spectra for a series of ENR products of various epoxide contents. The i.r. spectra of ENR are characterized by the presence of a specific epoxide band at $870\,\mathrm{cm^{-1}}$ (asym. epoxide ring stretching [14] beside a characteristic band of cis-ethylene at $840\,\mathrm{cm^{-1}}$ [14]. Variation of these bands, together with the other characteristic bands for epoxide ring and double bond, with epoxide contents was studied previously [16]. As seen from Fig. 6, the pure ENR derivatives show no presence of OH, CO or other side groups (curves 1–3). The ENR products obtained at high molar AcOOH/IP ratio in long lasting and/or in high acidic medium can show the presence of side ring-opening products (associated hydroxyl at 3200–$3600\,\mathrm{cm^{-1}}$, carbonyl ester at
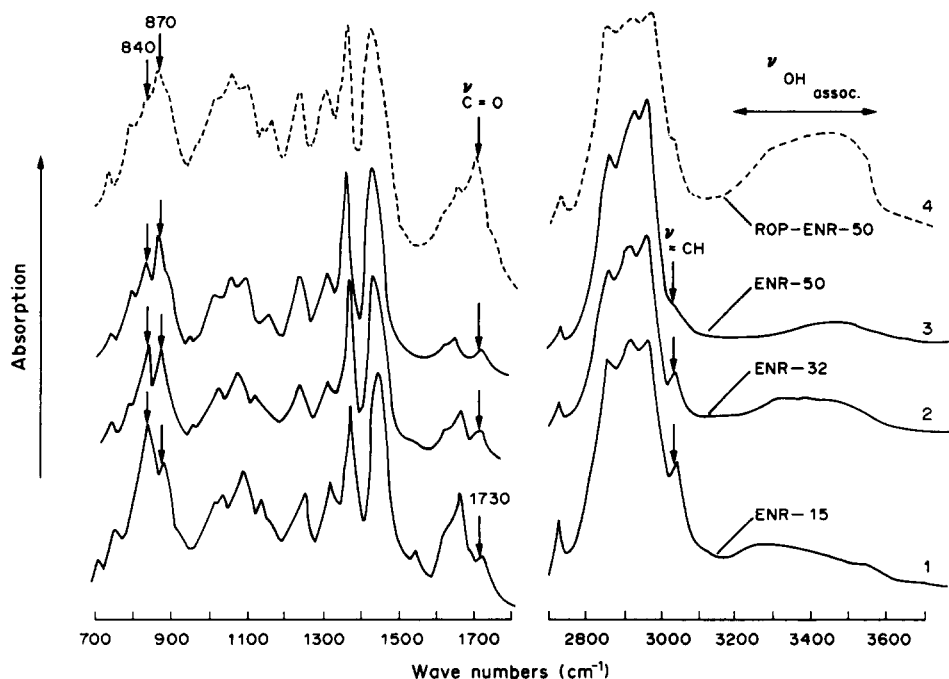

Fig. 6. Characteristic i.r. spectra for ENR of 15, 32 and 50 mol% epoxide groups (ENR-15, ENR-32 and ENR-50, curves 1—3, respectively) and an ENR-50 sample with particularly ring-opened product (curve 4, dotted line).
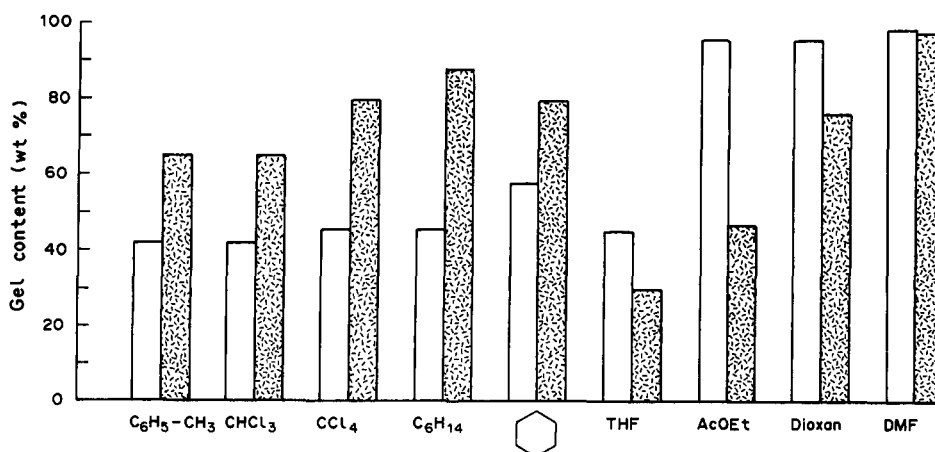
Fig. 7. Gel content (nonsoluble fraction) of NR and ENR-20 in various solvents.

1730 cm^{-1} and a cyclic ether band in the region of 1070–1100 cm^{-1}) as illustrated in Fig. 6, curve 4.

In ^{1}H-NMR, ENR samples show typical peaks for double bonds and epoxide rings at 5.08 and 2.70 ppm, respectively and no presence of specific peaks for diols (3.2 and 1.03 ppm) or cyclic ether (3.9 and 1.1 ppm) [17].

The epoxidation introduced groups of high polarity into the polymer backbone, increasing the polarity of the polyisoprene, leading to new interesting properties. The solubilities of a moderate ENR product (ENR-20, having 20 mol% epoxide group), as compared to the original NR in various solvents of different polarities, is presented in Fig. 7. Even at moderate level of modification, there is a clear difference between NR and ENR. As a nonpolar material, NR is more soluble in nonpolar or weakly polar solvents (chloroform, carbon tetrachloride, hexane etc.) while ENR-20 is more sensitive to polar solvents showing better solubility in tetrahydrofuran (THF), dioxane, ethyl acetate etc. (see Fig. 7). The influence of epoxidation level on the solubility was studied by comparison of the swelling capacity of NR and various ENR products in the presence of a nonpolar solvent (cyclohexane) at room temperature (see Fig. 8). The product of higher epoxide content clearly shows better resistance compared with NR and other ENR samples of lower epoxide contents. Figure 8 shows that the order of swelling decreases from NR, ENR-10, ENR-25 to ENR-50.
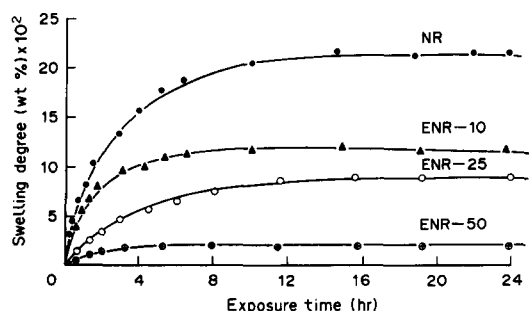
The epoxidation in latex also leads to increase of the gel content (nonsoluble fraction) of ENR as compared with NR, particularly at higher epoxide levels (at epoxide content > 55–60 mol%), as already observed also for in situ epoxidation by performic acid [7], as well as for reaction by peracetic acid in the presence of HCl [6]. The formation of gel is probably due to intermolecular side reactions which lead to partial crosslinking in parallel with the epoxidation. Further study to clarify the mechanism of gel formation and the contributing factors is necessary to prevent and/or to control the formation of the nonsoluble fraction during epoxidation.

CONCLUSIONS

NR latex stabilized by 1.65–5.0 phr nonionic surfactant [of the (fatty alcohol)/(ethylene oxide) condensate type] having up to 54% drc can be acidified by acetic acid to pH = 4, while retaining good aggregative stability.

Stabilized latex of medium-to-high drc (25–48%) could be successfully epoxidized at moderate temperature using preformed peracetic acid. The epoxidation proceeded rapidly and effectively, leading to ENR products free of side ring-opening groups. The ENR samples analysed by i.r. and ^{1}H-NMR show pure structures with up to 60–70 mol% of epoxide groups. Samples of ENR and NR compared by swelling and sol-gel determination showed that the epoxidation reduced the solubility of NR in nonpolar solvents and increased its sensitivity to polar solvents. The long lasting and high acidic medium of reaction in latex also increased the gel content of the product as compared with the original NR.

Fig. 8. Variation of swelling degree in cyclohexane of NR and some characteristic ENR samples having different epoxide contents.

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