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SYNTHESIS AND APPLICATION OF EPOXIDIZED NATURAL RUBBER

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ABSTRACT

North Vietnamese NR latexes were successfully epoxidized using peracetic acid at moderate temperature and pH range. The epoxide contents of pure epoxidized natural rubber (ENR) are from 5 to 70 mol%. The ENR products were characterized and determined by spectral and thermal analysis besides the chemical titration. Conditions of long-lasting or excessive temperature, or high acidic pH led to side ring opened products, proved easily by IR, ^{1}H-NMR, and DSC analysis. The ENR were vulcanized using a semiefficient system. The epoxidation increased the adhesion between rubber and tire cord and metal. This effect becomes stronger beyond 25 mol% and tends to be limited at over 60 mol%. The ENRs were used to formulate special-purpose adhesives. The shear strength of the adhesive ranges from 32 to 45 kg/cm^2 for bonding rubber to nylon and rubber to metal, respectively.

INTRODUCTION

Natural rubber (NR) is one of the important natural resources of Vietnam. The productivity of NR in Vietnam is approx. 70,000 tonnes (1994). The great majority of rubber products in Vietnam are made from NR. Research on the chemical modifications of NR for special technical applications has been begun recently in Vietnam. Among many reactions acting on the polyisoprene backbone, epoxidation is a modern and efficient method of chemical modification having great perspectives for application [1]. The epoxidation process introduces into the rubber backbone a new and very reactive group with great possibilities of further modifications.

This paper presents some results on syntheses and application of epoxidized natural rubber (ENR) directly from Vietnamese latex.

EXPERIMENTAL

Materials

The NR latexes used for study were full ammonia stabilized, prepared from latex collected in North Vietnam (Nghe An and Thanh Hoa provinces); and having dry rubber contents from 31.5% to 38.4% and total solid contents from 33.2% to 40.6%.

- Surfactant: fatty alcohol ethylenoxyde condensate
- Acetic anhydride (Ac_2O) (pa) of Cica (Kanto), Japan
- H_2O_2 50% purum (Warrington, U.K.).

All other solvents and chemicals were used as supplied.

Procedure

Peracetic acid was synthesized from Ac_2O and H_2O_2 at 35°-38°C. From 50% H_2O_2 can be obtained peracetic acid of 28-33% by weight. The NR latex was stabilized by a necessary amount of nonionic surfactant, as usual [2].

The epoxidation procedure was presented in detail previously [2, 3]. The latex samples were taken at intervals and the epoxide contents were determined by direct titration [4], or by spectral analysis as already shown [2, 5]. The T_g of ENR was determined by different scanning calorimetry (DSC) technique [6] using the onset value. The ENR compositions were mixed on a two-roll mill.

Infrared (IR) spectra were recorded on a Shimadzu IR-470 spectrometer. Nuclear magnetic resonance results (^{1}H-NMR) were recorded on a Jeol NMR-100 apparatus using a $CDCl_3$ solution. T_g were determined by a DSC-2C apparatus. Shear and peel tests were measured using a Zwick 1445, using standard methods [ASTM D-816 and BS-5350 (79)].

RESULTS AND DISCUSSION

Study on Raw Materials

The investigation uses latexes of natural rubber cultivated in North Vietnam. The main technical data of raw materials were studied and measured as follows.

Depending on the season and region of cultivation, the total rubber content varies in relatively large ranges, but the dry rubber contents and acetone extracts are within normal limits. It is seen that the total solid content (TSC) and dry rubber content (DRC) of latex from Nghe An Province (NA) are much lower than that of latexes from Thanh Hoa Province (TH). The reason for this difference is the fact that the NA latex was collected in the rainy months (Table 1).

TABLE 1. Main Technical Specifications of North Vietnamese Latexes

Technical specification	Sample Nghe An (NA)	 Thanh Hoa (TH)	 Creaming NA latex[a]	Test Method
Total solid contents (%)	33.1-34.7	39.3-40.6	61.5-61.8	BS-902-40
Dry rubber contents (%)	31.5-32.2	37.3-38.4	59.8-60.2	BS-902-40
Alkalinity (NH_3) %	0.91 ± 0.01	0.89 ± 0.021	0.945 ± 0.015	ASTMD-1076
Acetone extract (%)	2.08 ± 0.03	2.23 ± 0.03	3.41 ± 0.042	

[a] Latex was concentrated by creaming method, using Na alginate.

In our program of research, all three types of latex were used and successfully epoxidized. This paper shows in detail only our results performed with the TH latex.

Epoxidation of NR Latex

For epoxidation, the original latex was stabilized by nonionic surfactant (1-10 phr), diluted to 20-25% drc, then acidified by 50% aqueous AcOH to a suitable pH. Using peracetic acid, the optimal range of pH is from 4.2 to 5.5.

The conditions for synthesis and preservation of peracetic acid were studied systematically. Due to its high reactivity, the peracetic acid is self-degradable at room temperature, reducing its active oxygen content. Figure 1 shows the variation of acidic contents during conservation at 27°C and −10°C. It is seen that the peracetic acid is really unstable even at very moderate tropical temperature (in Vietnam, the average temperature yearly is 24°C (North) and 26°-27°C (South).

For long-lasting conservation of peracetic acid, it is necessary to maintain low temperature conditions. At low temperature (−10°C), the rate of decomposition is approx. 0.7%/month. In the hot summer months (t = 35°-40°C), the peracid is stable for only 2-3 days.

The stabilized latex was epoxidized by slowly pouring peracetic acid into it under continuous stirring.

Characterization of ENR

The ENR samples are white to off-white in color. The hardness of ENR increases with its epoxide contents. However, samples of low degree of transformation (below 20-25 mol%) are as elastic as NR. The infrared (IR) spectral characteristics of ENR having different epoxide contents were studied in detail in one of our previous papers [5]. The peak assignments for NR and some derivatives of ENR are shown in Table 2. IR spectra were used also to determine ENR [2, 5].

When the reaction proceeds at high temperature (>40°C), in high acidic medium and/or for a prolonged time, a medium to strong band of cyclic ether at 1070 cm^{-1} appears in the spectra. This band was assigned to a tetrahydrofuran (THF) ring formed by a ring-opening side reaction [5, 6]. At higher epoxide contents, a weak band appears at 807 cm^{-1} due to the epoxide ring deformation. In this

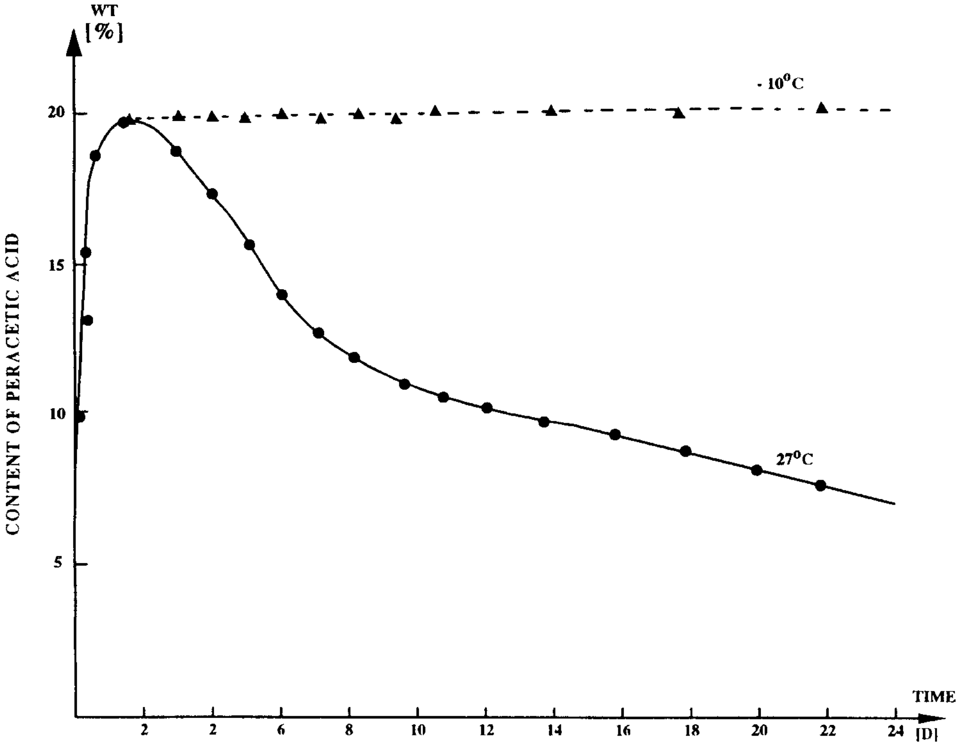

FIG. 1. Variation of peracidic content during conservation at 27°C and at −10°C.

way, the IR spectra can serve to identify various intermediates and products of different epoxide levels. The method makes it possible to visualize the epoxidation process readily, offering useful information for a rapid and simple examination.

The epoxide content and the rate of reaction depend strongly on the peracid/isoprene ratio as well as on the reaction temperature. The epoxidation is also very sensitive to pH. At low pH values (pH < 4), the reaction proceeds very quickly and the system could be easily coagulated suddenly! The products obtained under low pH, high temperature, and long-lasting conditions present ring-opened components as proved by IR spectra (stretching band of OH groups at 3200–3580 cm^{-1}, $\nu_{\mathrm{E}=\mathrm{O}}$ at 1720–1740 cm^{-1}, $\nu_{\mathrm{C}-\mathrm{O}}$ at 1070–1080 cm^{-1}), or by DSC thermogram (broadening the phrase transfer range Δt from 10°C to 20°–25°C and making this jump less sharp).

The moderate conditions of reaction (t < 20° C, pH = 4.5–5.5, and peracid/isoprene ratio from ~0.1 to 0.80 M/M) allow the process to be correctly controlled and lead to pure ENR products, having epoxide contents from 5 to 75 mol%.

At 20°–25°C, the epoxidation is effectively fulfilled in 120–150 min. The reaction is fastest in the first 60 min and tends to a stationary region after approx. 2 h. Parallel with researches with latex, we have carried out the epoxidation in solution, also. This method uses NR crepe, roll milled to reduce MW and increase its solubility in xylene. The reaction was performed as already shown [7]. The studies showed that at the same initial peracid/isoprene ratio, two methods lead to similar

TABLE 2. Peak Assignments for NR and Its Derivatives[a]

Wave-number	Functional group	Assignment of band	*cis*-1,4-PI (NR)	ENR	Ring-opening product
3450	Hydroxyl	ν_{OH}			3200-3580
3040	*cis*-Alkene	$\nu_{-\mathrm{CH}}$	3040 (m)	3040 (w)	3040 (sh)
2960	Methyl	CH_3	2965	2965	2970
2924	Methylene	CH_2 (asym)	2925	2925	2940
2850	Methylene	CH_2 (sym)	2850	2850	2870
2720	–	Nonassigned	2725	2725	2725
1740	Ester carbonyl	$\nu_{\mathrm{C-O}}$	1740 (vw)	1740 (w)	1740 (s)
1710	Carbonyl	$\nu_{\mathrm{C-O}}$	1710 (vw)	–	–
1665	*cis*-Alkene	$\nu_{\mathrm{C-C}}$ or Me—C=CH—	1665 (m)	1665 (mw)	1665 (sh)
1640	*cis*-Alkene	$\nu_{\mathrm{C-C}}$ or CH_2=C—Me	1640 (sh)	1640 (sh)	1645 (sh)
1460	Methylene methyl	δCH_2 (sc) δCH_3 (asym)	1455	1455	1455
1070	Tetrahydrofurane	Ring str.	–		1070 (s)
1040	Methyl	$\delta_{(\mathrm{ip})}CH_3$ (r)	1040	1040	1040 (sh)
870-880	Epoxy ring	Asym. str.	–	875	–
860	Alkene	C=CH_2			860 (w)
835-840	*cis* MeC=CH—	$\delta_{(\mathrm{oop})}$CH	835-840 (s)	840 (mw)	840 (sh)
807	Epoxy ring	Ring deform.		807 (w)	
760	*cis* Me—C=CH—	Me—C	762		
740		=CH—	742	750	740 (vw)
720	Methylene	CH—(r)	–	720	720
600	C—Br	$\nu_{-\mathrm{Br}}$			
570	*cis*-Alkene	Unspecified	572 (m)	572 (w)	572 (sh)
520		Nonassigned	520	520	525 (w)

[a] Extracted from Ref. 5. Abbreviations for intensity: s—strong, m—medium, w—weak, mw—medium to weak, vw—very weak, sh—shoulder. Abbreviations for type of vibration: sym—symmetrical, asym—asymmetrical, t—twisting, r—rocking, sc—scissoring, str—stretching (ν), ip—in-plane deformation (δ_{ip}), oop—out-of-plane deformation (δ_{oop}).

epoxide contents and the same final conversion. The rate of epoxidation in solution did not strongly exceed the rate in latex medium, which justifies the technological advantages of the latex method (using higher dry rubber contents, avoiding high consumption of energy and solvents, absence of fire and pollution hazard).

The ^{1}H-NMR spectra of ENR samples were recorded on CDCl, solution and could be used to characterize the product both qualitative and quantitative [2, 3, 6]. The presence of a proton at the epoxide group is observed at δ = 2.68-2.69 ppm, besides other important peaks (δ = 1.28 ppm; $C\underline{H}_3$—CO; δ = 1.65 ppm; $C\underline{H}_3$—C=C; δ = 2.1 ppm; —C$\underline{H}$—: δ = 5.10 ppm; C$\underline{H}$=C) [8-10].

For ring-opened products, there are also other peaks at δ = 3.3-3.4 ppm (diol or Hα to HO) and at δ = 3.9 ppm (furane) [11].

The introduction of a epoxide group into the original NR backbone leads to increased glass temperature (T_g). The relationship between the T_g and the epoxide

TABLE 3. Comparative Data of Epoxide Contents Determined by Independent Methods (mol%)

No.	IR	^{1}H-NMR	DSC	Value of $T_g{}^a$ (°C)
1	5.5	6	5	− 6.3
2	8.2	—	8.5	−60.5
3	11.5	11.5	11	−58
4	16	16.6	16	−54.5
5	25.5	24	25	−47
6	35.1	36.5	36	−37
7	48	50	49	−26
8	62	68	66	−12
9	—	72	75	− 5

$^a T_g$ values are onset temperatures.

contents was found to be linear and univocal. It could be used as a standard for determination of ENR. (The samples must be checked beforehand for pure structure by IR or by ^{1}H-NMR spectra.) The results of determining epoxide contents by different methods are shown in Table 3. It is seen that the epoxidation has increased the T_g by ~0.96 K/mol%.

Vulcanization and Application of ENR

It is known that the normal curing systems are not suitable for ENR.

The ENR was vulcanized at 148° ± 2°C/30 min using the following systems: the appropriate rubber 100 p, ZnO 5–8 p, stearic acid 2 p, antioxidant 1 p, S 1.5–2 p, accelerator (sulfenamide type) 0.6–2 p, processing oil 3 p, HAF carbon black as required, and other minor components. The ENR tested for adhesives have epoxide

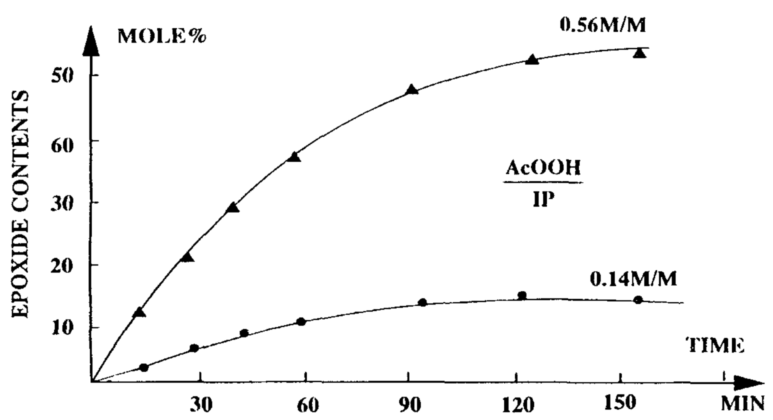

FIG. 2. Variation of epoxide contents during epoxidation. Reaction conditions: T = 20°C, pH$_0$ = 4.5.

contents from 10 to 70 mol%. The study on adhesion by the peel test showed that under 20 mol% of epoxidation there is only small improvement of adhesion. The significant increase of adhesion occurs at 25–30 mol% of epoxide and tends to be limited at 65–70 mol%. The shear strength of the adhesive bond between rubber and nylon (tire cord) tested at room temperature can reach 36–38 kg/cm^2. Using a suitable primer based on a phenolic resin and ENR-50 it is possible to formulate a good rubber-to-metal adhesive having shear strength as high as 40–45 kg/cm^2.

From ENR-35, the technical specifications of a typical rubber-to-tire cord (nylon) adhesive are:

1.	Dry content	17–19%
2.	Viscosity (V-Z-4 cup)	150–160 sec
3.	Density (g/m^3)	0.885–0.895
4.	Shear strength (kg/cm^2)	36 ± 2
5.	180° peel strength (N/cm)	55–65

CONCLUSION

North Vietnamese NR latexes can be successfully epoxidized using peracetic acid at moderate temperature and pH values. Conditions of long-lasting or excessive temperature, or high acidic pH led to side ring opened products. The epoxidation increased the adhesion between rubber and tire cord and metal. This effect increases above 25 mol% ENR and tends to be limited at over 60 mol%. The ENRs can be used to formulate special-purpose adhesives.

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