Surface Modification of Natural Rubber Laces

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Synopsis

Epoxidation has been applied to modify the surface of natural rubber laces. When very thin laces of fractionated bleached rubber are used, about 6% of the double bonds could be modified. Using ^{1}H nuclear magnetic resonance (NMR) and infrared (IR) analysis the best condition for the reaction was worked out. Both ^{13}C NMR and differential scanning calorimetry (DSC) results indicate that the 6% epoxide groups are placed in a predominantly block manner. Modification in yellow fraction rubber however gives lower epoxy contents. Increase in glass transition temperature by epoxidation results in more damping and better abrasion resistance. The resultant polymer acts very similar to a 90/10 natural rubber/50% epoxidized natural rubber (NR/ENR-50) blend.

INTRODUCTION

Natural rubber latex (Hevea Braseliances) contains carotenoids as a non-rubber substance, and these compounds should be removed to obtain the water white color in latex crepe rubber. One method of removing the carotenoid pigments from latex is by fractionation. In this process nearly 10–15% of the rubber is coagulated with the carotenoids, and this 10–15% is processed as yellow fraction which is yellow in color. This yellow fraction (YF) according to the greenbook grading falls into an off grade which fetches a very low price. There are other grades of off-grade, low-quality crepe rubbers produced using field scrap. This is the rubber which is allowed to undergo bacterial coagulation. Nearly 20,000 MT of these two off grades are produced annually in Sri Lanka.

An attempt was made to modify the surface of these rubbers and upgrade them, and the results are presented in this paper. Epoxidation of the natural rubber[1-3] double bond is one of the chemical modifications which are now receiving commercial acceptance, since it presents some exceptional properties.[4] Epoxidation of natural rubber has been carried out in solution[1] and in latex.[2,5] In general, any desired epoxidation level can be achieved. Epoxidation has been shown to improve such properties as oil resistance, gas permeability, wet grip, rolling resistance, and abrasion resistance,[6] so that natural rubber could compete with some synthetics. For example, ENR-50 (50% epoxidized natural rubber) has oil resistance comparable to that of medium content nitrile rubber and air permeability comparable to that of butyl rubber.

EXPERIMENTAL

Preparation of Epoxidized Rubber

Fractionated bleached rubber (FB) with 0% gel content or YF or scrap crepe wet laces of thickness ·30 mm were soaked in solutions of hydrogen peroxide,

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formic acid, and water. This treatment was carried out at different temperatures (40°C and 50°C) for different durations of time (2, 4, 6, 8 h), at the end of which the rubber samples were washed thoroughly with water, 10% sodium carbonate solution, and again with water until the pH was neutral. The rubber was then dried at 34°C. The rubber was also epoxidized in latex or in organic solutions according to reported methods.[1,2,5]

Methods

NMR Spectroscopy. ^{1}H NMR spectra were obtained at 200 MHz and proton decoupled ^{13}C NMR spectra were obtained at 50 MHz using a Joel Fx 200 spectrometer with an Oxford Instrument Co. Magnet. For the ^{13}C NMR spectra free induction decays were accumulated in 16K data points, spectral with 15,000 Hz, 13 Ms(45°) pulse width, and 3s repetition time. Spectra were determined at 298 K in $CDCl_3$ (5% wt/vol) with TMS as an internal standard. The amount of epoxidation was calculated as previously discussed.[7,8]

IR Spectroscopy.[9] Infrared (IR) spectra were obtained using a Perkin Elmer model 377 spectrometer. Samples of dry ENR were generally dissolved in chloroform and films cast directly into sodium chloride plates from the resulting solution. On occasion, however, when the samples had a high gel content it was necessary to press them between two sodium chloride cells.

Differential Scanning Calorimetry.[9,10] A Perkin Elmer differential scanning calorimeter (DSC-2B) fitted with a liquid nitrogen cooled subambient accessory was used to relate the shift in glass transition temperature (T_g) relative to natural rubber. Dried samples (10 mg) were encapsulated in aluminium pans, heated to 150°C at 320°C/min, cooled to -100°C at the same rate, and then heated at 20°C/min through the T_g in an atmosphere of helium. The instrument was calibrated as described elsewhere.[11]

Raw Rubber Properties. The raw rubber properties (initial Wallace plasticity, plasticity retention index, nitrogen, Mooney viscosity, and Lovibond color) were determined according to standard method used in technically specified rubbers.

Technological Properties of Vulcanized Rubber. Mixing of the chemicals was conducted in a Laboratory Banbury at 116 rpm starting at 50°C using the following mix cycle.

0 min- Load rubber and sodium carbonate (where applicable)
1 min- Load powder ingredients (zinc oxide, stearic acid, antioxidant, etc.)
$1\frac{1}{2}$ min- Load 1/2 black + process oil
$2\frac{1}{2}$ min- Load remainder of black
$3\frac{1}{2}$ min- Sweep
4 min- Dump

In all cases, sulfur and accelerators were added later on a two-roll mill and the test specimens were cured to 95% cure at 150°C. The cure times were calculated using a Monsanto Rheometer 100. Physical testing procedures were standard as follows:

Tensile strength to ISO 37 using Instron
Hardness to ISO 48 (ASTM D 1415)

Resilience using Lupke pendulum to BS 903 Part A8

Compression set to ISO 815 (ASTM D 395)

Heat build up, Goodrich flexometer to ISO 4666/3 (ASTM B 623 method A)

Abrasion DIN to ISO 4649

Ageing to ISO 188 (ASTM D 573)

Volume swelling to ISO 1817 (ASTM D 471)

RESULTS AND DISCUSSION

Initial trials were carried out using freshly prepared FB crepe rubber laces of thickness ·30 mm with no gel content so that differential fractionation of the modified rubber was easy. The wet rubber laces were soaked in different solution mixtures shown in Table I.

When composition 1 was used the temperature increase was rapid and at one instance the rubber caught fire. Therefore, the samples from this trial were discarded without analyzing. Samples drawn from the other trials were analyzed using ^{1}H NMR and IR spectroscopy.

^{1}H NMR and IR Spectroscopy Analysis

^{1}H NMR spectra of the initial samples (2 and 4 h) of compositions 2 and 3 (reacted at 40°C) did not indicate any reaction though samples had a very

TABLE I

Compositions[a] of Chemicals Used in the Trials and the Analysis of the
Gel Fractions of the Products[b] Using ^{1}H NMR

	Moles/mL			Analysis of the product after 8 h reaction			
Composition	Hydrogen peroxide	Formic acid	Maximum epoxy[c] content reacted (%)	Double bond	Epoxy groups	Furan groups	Hydroxyl groups
1	0.01	0.004		—	—	—	—
2	0.008	0.0031	24(4 hrs)	47	—	46	7
3	0.008	0.0027	31($4\frac{1}{2}$ hrs)	46	11	38	5
4	0.008	0.0019	47($7\frac{1}{2}$ hrs)	43	48	8	—
5	0.006	0.0019	56(8 hrs)	44	56	—	—

[a]200 g of rubber was immersed in 560 mL of these solutions.
[b]Reactions carried out at 40°C.
[c]The figures in brackets indicate the time of which this maximum is reached.

TABLE II

The Assignment of ^{1}H NMR Spectra

Group	^{1}H NMR chemical shift (ppm)	IR absorption (cm^{-1})
Olefin	5.08	—
Oxirane	2.68	835
Furan	3.90	1065
Hydroxyl	3.40	3200–3600

different physical appearance. The samples drawn toward the end (6 to 8 h) were harder and the rubbery appearance had disappeared. A very small peak at 3.9 ppm was visible in the ^{1}H NMR spectra of these samples. However, when these samples were dissolved in benzene, a gel fraction of about 10% could be separated easily. The sole fraction was unreacted rubber but the gel fraction contained epoxy groups, hydroxyl groups, furan and higher membered cyclic structures as indicated by the ^{1}H NMR peaks at 2.68, 3.4, and 3.9 ppm, respectively (see Table II).[2,7,8,12] These products are expected from the ring-opening reactions of epoxy groups when exposed to high acid concentrations.[12]

The ether linkages between epoxy groups in two rubber molecules cause a crosslink. A very small number of such crosslinks is sufficient to give a gel fraction and are normally too low to be visible in the ^{1}H NMR spectra.[12] The number of epoxy, hydroxyl, and furan groups in the product after 8 h of reaction, as well as the maximum epoxy content reached with each composition, is given in Table I. Accordingly, in composition 2, the epoxy content of the gel fraction reached only a maximum of about 24% and then dropped due to the formation of ring-opened products. The presence of gel fraction in the initial samples (2 and 4 h) indicated that the ring opening of the epoxy group commences at an early stage as a result of the high formic acid concentrations. The 24% of the 10% gel fraction is only 2.4% of the total reaction product and this is the reason why it was not shown in the ^{1}H NMR of the unseparated sample. However, the furan content in the gel fraction of the final sample is nearly 50%, which is 5% in the unseparated sample and thus a peak at 3.9 ppm was visible in the corresponding ^{1}H NMR spectrum. These results were confirmed by IR spectra,[9,13] which have been assigned before (see Table II).

The ^{1}H NMR spectra of the unseparated samples from compositions 4 and 5 collected toward the end of the reaction (6 and 8 h) show an epoxy content of about 6%. The first few samples of these trials did not show any new peaks. The samples collected at 6 and 8 h from composition 4 and sample collected at 8 h from composition 5 gave a 10% gel fraction, indicating a ring opening and ether linkage formation in these products. The gel fractions separated from these samples were 56% epoxidized rubber while the corresponding sol fractions were unreacted rubber. None of the other samples drawn from compositions 4 and 5 had a gel fraction, thus the separation of these samples were difficult. According to these results, only compositions 4 and 5 resulted in products with the minimum amount of epoxy ring-opening reactions. Compositions 4 and 5 when carried out at 50°C resulted in products with higher gel contents and lower epoxy contents but other epoxy ring-opened products. Therefore, composition 5 reacting at 40°C was selected as the best reaction conditions for the purpose of the reaction. This will result in a polymer mixture with 90% unreacted rubber and the balance of 56% epoxidized rubber. The only secondary reaction is the very small amount of ether linkages as evident from the presence of the gel. However, the 90% sol fraction could contain molecules with very few epoxy groups.

^{13}C NMR Spectroscopy Analysis

The product (composition 5; 8 h) was then analyzed with ^{13}C NMR spectroscopy. The peaks in the ^{13}C NMR spectra of partially epoxidized

TABLE III
Percentage of Occurrence of Triad Sequences in Gel Fraction of the Surface-Epoxidized
Natural Rubber, Solution, and Latex Epoxidized Natural Rubber

Triad sequence	Resonance (ppm)	Level of epoxidation		
		56 gel fraction of the surface-modified product	54 latex method[a]	64 solution method[a]
CEC, CEE	33.21	12	21	22
CCC	33.24	20	8	4
CCE	32.11	18	10	7
EEC, EEE	29.73	37	28	44
ECC, ECE	28.78	13	27	23
Number-average sequence length of epoxy groups		4.0	2.0	2.6

[a] From Ref. 3.

rubber had been assigned previously,[3] and the methyl and methylene regions of this ^{13}C NMR spectra used to study the microstructure of the partially epoxidized product. The sequence distribution of the triads between epoxidized and unepoxidized isoprene units (calculated using the peak intensities as has been done previously)[3] of the gel fraction of the surface-modified product and for comparison that of solution and latex modified products are given in Table III. The results indicate that the surface modified product has higher percentages of triads CCC and EEE than that in the solution and latex epoxidized products, which has random distribution of epoxidized (E) and unepoxidized (C) isoprene units.[3] This indicates that the surface modified product is a predominantly block copolymer, confirmed by the higher number-average sequence length of epoxy groups. Such a block copolymer has been obtained in 1,4 polybutadiene, when the crystals of this polymer in a suspension are reacted with a peracid.[14] In that case, only surface folds had reacted completely and the crystal stems had not reacted at all, leading to a block structure. It is fair to expect a similar situation in the present system too. It is known, however, that dry natural rubber when soaked can absorb water.[15] Therefore the performic acid in the mixture could be absorbed into and react with the molecular parts inside. But the amount of water that could be absorbed within 8 hours is very small. Thus even if the "internal" double bonds are reacted, it is only to a very small extent.

Differential Scanning Calorimetry

As has been disclosed previously[2,16,17] the glass transition (T_g) of ENR varies linearly with epoxy content. Therefore T_g measurements have been used[17] to detect and estimate blends of epoxidized natural rubber and natural rubber. A thermograph of the unseparated sample from composition 5 was found to be the same for that of natural rubber (shown in Fig. 1). Only a
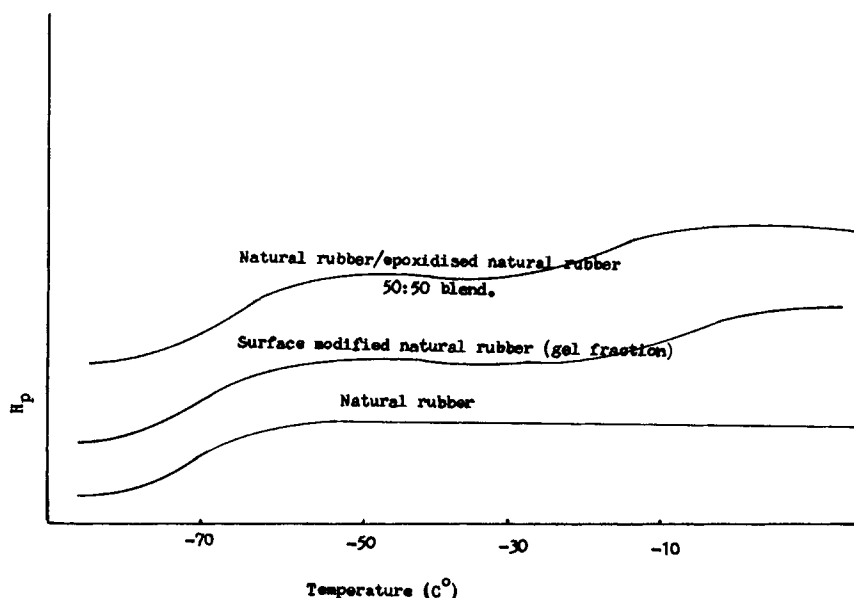
Fig. 1.   Differential scanning Calorimetry curves of the rubbers.

deflection at $-67°C$ was observed, which is due to the glass transition of natural rubber.

As measured by ^{1}H NMR, the amount of epoxidized rubber present in this is only 5.6%, and since glass transition is a very small deflection it could be expected that the glass transition of epoxidized rubber component in the sample could go undetected. A thermograph of the gel fraction (56% epoxidized) of the same sample showed two distinguishable deflections at $-69°C$ and $-10°C$. A 60% randomly epoxidized natural rubber sample should give a single glass transition at about $-20°C.$[9,10] However, it is known that the block copolymers have two glass transition temperatures corresponding to the two components of the copolymer. The deflection at $-69°C$ is the glass transition of the natural rubber component and the one at $-10°C$ may be that of epoxidized component. Thus the DSC results confirm the observation from ^{13}C NMR, that the gel fraction contains a predominating block copolymer.

Raw Rubber Properties

The structural analysis discussed above was done on the products obtained from FB rubber. Once the structure is established it is our aim to apply these surface modifications to off-grade rubbers. Therefore, the properties discussed below will be on modified products from YF rubber. The epoxy content of the surface-modified product (composition 5, 8 h) from YF rubber was only 4%. This low level in YF rubber could be due to higher protein content in the YF which obstruct the reaction of double bond with peracids. Due to the presence of gel (storage hardening of rubbers[18] due to the presence of higher level of nonrubber substances) in the original rubber itself, it is not possible to separate this product, as was done with the FB rubber. The raw rubber

TABLE IV
Raw Rubber Properties of the Surface-Modified Yellow Fraction Rubber

	P_o	PRI	V_r	Color	Nitrogen (%)	Density (g/cm³)
Control[a]	55	80	110	6.0	.60	0.89
Product 1[b]	46	27.4	90	3.0	.37	0.94
Product 2[b]	50	66.0	98	3.0	.40	0.96
Product 3[b]	53	79.7	105	3.0	.41	1.10

[a] Yellow fraction rubber.
[b] Product 1, 2, 3 are the surface-modified products obtained from compositions 2, 4, and 5 reacted at 40°C for 8 h.

properties namely: Wallace plasticity (P_o), plasticity retention index (PRI), Mooney viscosity (V_r), Lovibond color, nitrogen and density are given in Table IV. Product 1 (which contain many secondary reaction products) has the worst raw rubber properties, especially the very low PRI which is a measure of the oxidizability. Product 3 has the best balance of raw rubber properties, and this is in accordance with our observation that it is a clean product with minimum side reactions. P_o and V_r which are related to the molecular weight should increase with crosslinking. In YF, which already contains crosslinks the very small degree of crosslinking due to epoxy groups has not contributed significantly to P_o or V_r. Nitrogen content of the rubber has dropped during modification and this may be a result of hydrolysis of protein by hydrogen peroxide. The yellow color of the product disappears with the peracid treatment as a result of the epoxidation of conjugated double bonds in the carotenoids by the peracids.

Processing Characteristics and Vulcanizate Properties

During processing, products 2 and 3 behaved essentially like natural rubber. Band on the mill was easily formed and the incorporation of the curatives was

TABLE V
Cure Formulations Used

	Semi-EV	EV
Rubber	100.0	100.0
Zinc Oxide	5.0	5.0
Stearic acid	2.0	2.0
MOR[a]	1.5	2.4
TMTD[b]	—	1.6
PVI[c]	0.3	0.2
Carbon black	30.0	30.0
Oil	5.0	5.0
Sulfur	1.5	0.3
Sodium carbonate[d]		

[a] 2-(Morphilinothio)Benzothiazole.
[b] Tetramethyl thiuram disulfide.
[c] Prevulcanize inhibitor.
[d] Sodium carbonate was not used when cure characteristics are measured.

TABLE VI
Cure Characteristics (at 150°C) and the Physical Properties of the Rubber

	Semi EV			EV		
	Yellow fraction	Modified yellow fraction (Product 3)[a]	NR/ENR-50 (90/10) blend	Yellow fraction	Modified yellow fraction (Product 3)[a]	NR/ENR-50 (90/10) blend
Scorch time (min)	5	4	—	4	3	—
Optimum cure time, T_{95} (min)	24	25	—	45	47	—
Tensile strength (MPa)	33.6	32.2	31.8	27.0	25.6	25.4
Elongation at break (%)	660	680	680	580	600	600
Modulus at 100% extension (MPa)	1.5	2.0	1.9	1.5	2.0	2.0
Modulus at 300% extension (MPa)	7.9	8.5	8.8	7.9	8.9	8.9
Hardness (IRHD)	56	62	61	59	70	66
Dunlop resilience at 23°C (%)	73	54	57	73	63	68
Compression set, 24 h/70°C (%)	21	20	20	17	18	17
Goodrich HBU (5.71 mm stroke 11 kg load, 30 H_z for 30′($\Delta T°C$))	40	45	45	43	50	48
Akron abrasion (mm 3/500 rev)	22	18	21	44	42	42

[a] See Table IV.

easy in these two products. Product 1 tends to slip on the mill and toward the end was very sticky, the incorporation of the chemicals was very difficult.

It has been discovered that conventional cure systems based on 2.5 phr sulfur and 0.5 phr sulfenamide yield ENR vulcanizates with poor aging characteristics as compared to unmodified natural rubber.[19] The cause of this is believed to be a totally different aging mechanism, in which sulfur acids from the oxidation of sulfides promote ring-opening of epoxide groups to give large-membered rings which makes the product stiff. Therefore, semi EV and EV formulations (see Table V) had to be selected, and this same practice was followed in this work.

Cure characteristics as shown in Table VI are very much similar to the control (YF). Physical properties of the control and surface-modified rubber are also summarized in Table VI. The surface-modified rubber was also compared with a blend of NR/ENR-50 (90/10) since this blend has been found to be useful in tread and sidewalls of motorcycle tires.[20] It is found that the general properties of both the surface-modified rubber and the blend are similar to those of natural rubber. This is expected as low level of epoxidation is found to preserve many general properties of rubbers while having high damping capabilities.[2] Differences were expected in resilience and abrasion. The glass transition temperature of a polymer is known to have an important bearing on resilience. For example, polybutadiene with low glass transition is highly resilient, while SBR has a high glass transition, and thus exhibits low resilience.[20] This is also seen in rubbers epoxidized to different levels. The surface-modified product contains 10% of ENR which is a predominantly

TABLE VII
Aging of Rubber Vulcanizates (Semi EV Formulation)

	Natural rubber	Surface-modified rubber	NR/ENR-50 blend(90/10)
Aged 10 days at 70°C			
Retention (%)			
Modulus at 100%	140	156	160
Modulus at 300%	130	135	140
Tensile strength	93	90	92
Elongation at break	90	90	80
Hardness	110	105	105
Aged 3 days at 100°C			
Retention (%)			
Modulus at 100%	139	140	155
Modulus at 300%	127	125	125
Tensile strength	87	90	95
Elongation at break	88	89	85
Hardness	110	105	105

TABLE VIII
Swelling (% wt Increase) of Rubber Vulcanizates in Oils

Oil	Rubber		
	Yellow fraction	Surface-modified yellow fraction	NR/ENR: 90/10 blend
Brake fluid (14 days)	1	10	9
Engine oil (30 days)	126	60	66

block copolymer. This has a higher T_g value than the ENR-50 used in the blend. As a result the resilience of the modified product is even lower than that of the blend. The rubbers with lower resilience are expected to have low rolling resistance and low wet grip. Air aging properties of the surface-modified products are found to be similar to that of natural rubber and NR/ENR-50 blend, as shown in Table VII. Epoxidation is known to change the oil resistance of natural rubber. Due to the introduction of a polar oxygen group, the rubber swells less in nonpolar oils and swells more in polar oils. This is evident in Table VIII where normal brake oil (polar fluid) and engine oil (non polar fluid) are used as the swelling media.

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