Storage Hardening of Natural Rubber

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STORAGE HARDENING OF NATURAL RUBBER

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ABSTRACT

Natural rubber exhibits different storage properties when compared with synthetic polyisoprenes. Stored over an extended period of a few months, natural rubber is found to become progressively harder while the synthetic rubber is known to soften. This phenomenon of spontaneous crosslinking of natural rubber in storage is of considerable importance since it affects the processing properties. The process of storage hardening has been actively investigated and is believed to involve abnormal groups in the rubber molecules. This paper reviews the various proposals by different workers involving aldehyde, epoxide, and amino acids. Our recent results show that amino acids react with certain abnormal groups in rubber at the latex stage. The net effect of the reaction is to functionalize the rubber with carboxylic, hydroxylic, and amine groups in addition to the original abnormal groups. Storage of the dry rubber could lead to slow crosslinking reactions which are accelerated by anhydrous conditions.

INTRODUCTION

The progressive hardening that occurs in natural rubber on prolonged storage under ambient conditions leads to a considerable increase in Wallace plasticity and Mooney viscosity. This phenomenon affects the processing properties and has attracted much attention over the years [1, 2]. Although the technological problems have been overcome to a large extent [3], the mechanism by which this process occurs has yet to be clearly established since various aspects of the process are not completely reproducible in experiments. Investigation is complicated by clonal and

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seasonal variations of the rubber trees which affect the enzymes, amino acids, and minerals content of the latex. In addition, conditions of rubber isolation and storage also affect the rate and extent of hardening [4]. Although the crystallization process of natural rubber at low temperature causes hardening, the effect can easily be reversed by warming to "thaw out" the rubber whereas storage hardening is not reversible by thermal changes [5]. It is quite certain that storage hardening is not due to a change in the physical state of the rubber. There is general agreement that storage hardening is not a simple by-product of oxidative degradation and that certain abnormal groups probably provide sites for spontaneous crosslinking.

ALDEHYDE GROUPS IN NATURAL RUBBER

The postulate that rubber contains aldehyde groups was based on the observed inhibition of storage hardening by certain monofunctional amines, such as hydroxylamine 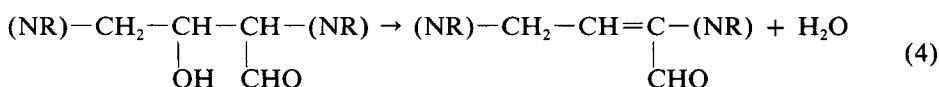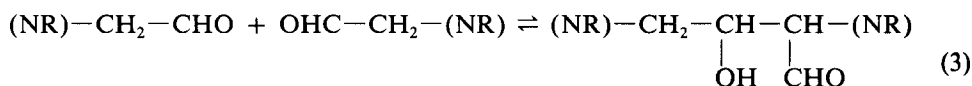and semicarbazide [6, 7]. The rubber molecules were also supposed to contain "aldehyde condensing groups" which could react with the rubber aldehydes. The ability of a bifunctional amine, such as hydrazine, to promote a hardening reaction was attributed to azine formation:

$$2(NR)-CHO + H_2N-NH_2 \rightarrow$$
$$(NR)-CH=N-N=CH-(NR) + 2H_2O \tag{1}$$
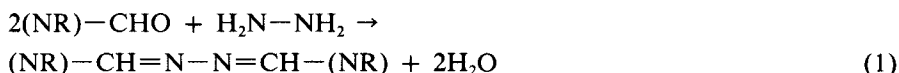
Monofunctional amines could inhibit crosslinking through the formation of aldoxime and imine:

$$(NR)-CHO + NH_2-R \rightarrow (NR)-CH=N-R + H_2O \tag{2}$$

To account for the fact that hardening was accelerated by conditions of low humidity, Sin [8] proposed a bimolecular aldol condensation between rubber aldehyde groups occurring in the dry rubber:

$$(NR)-CH_2-CHO + OHC-CH_2-(NR) \rightleftharpoons (NR)-CH_2-\underset{\underset{OH}{|}}{CH}-\underset{\underset{CHO}{|}}{CH}-(NR) \tag{3}$$

$$(NR)-CH_2-\underset{\underset{OH}{|}}{CH}-\underset{\underset{CHO}{|}}{CH}-(NR) \rightarrow (NR)-CH_2-CH=\underset{\underset{CHO}{|}}{C}-(NR) + H_2O \tag{4}$$

Gorton [9] used the same scheme for reactions in latex to explain the increase in the initial plasticity of rubber isolated from latices stored at high pH. In addition, he also reported that when a monofunctional amine was added to the latex in a small amount, it could cause significant crosslinking.

DISCOVERY OF EPOXIDE GROUPS IN NATURAL RUBBER

While investigating the chemical modification of rubber by epoxidation, HBr in glacial acetic acid was used to quantitate the extent of epoxidation [4, 10].

$$-CH_2CH=\underset{\underset{CH_3}{|}}{C}-CH_2- \xrightarrow{\text{peracid}} -CH_2CH-\underset{\underset{O}{\diagdown\diagup}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-$$

$$\xrightarrow{\text{HBr}} -CH_2\underset{\underset{H}{|}}{CH}-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2- \tag{5}$$
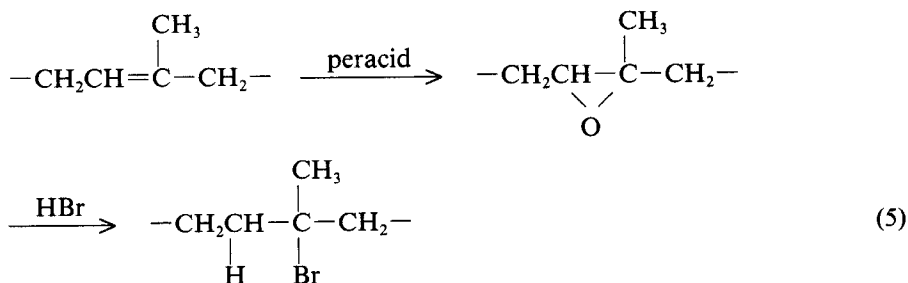
The untreated rubber (as a control) was found to contain 42 mmol epoxide per kg rubber (Table 1). Repeating the determination on a number of rubber samples from trees of different clones led to the conclusion that the rubber molecules contain small amounts of epoxide groups.

CROSSLINKING INVOLVING EPOXIDE GROUPS

Burfield [11] figured that the known biosynthetic pathways for isoprenoid compounds could not account for the presence of aldehyde groups in rubber, let alone aldehyde condensing groups, while epoxide groups have been found in numerous natural products. He suggested that the observed storage hardening of rubber could be due to reactions involving epoxide groups and naturally occurring amino compounds.

$$
\begin{array}{c}
\overset{\displaystyle CH_3}{\underset{\displaystyle O}{-CH_2-CH-\overset{|}{\underset{\diagup}{C}}-CH_2-}} + RNH_2 \rightarrow -CH_2-CH-\overset{\displaystyle CH_3}{\underset{RNH\ \ OH}{\overset{|}{C}}}-CH_2- \quad (I) \quad (6)
\end{array}
$$

$$
-CH_2-CH-\overset{CH_3}{\underset{O}{\overset{\diagup}{C}}}-CH_2-
$$
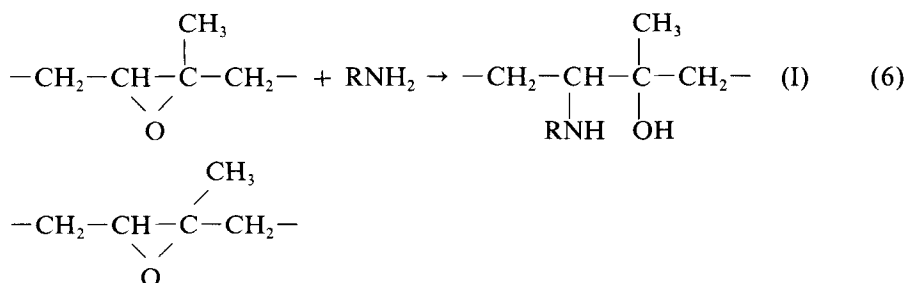
TABLE 1.   Determination of Epoxide Content
by HBr Titration [4, 10]

No.	Rubber	Epoxide content ($mmol \cdot kg^{-1}$ rubber)
1[a]	Epoxidized rubber	349
2[b]	Control (untreated)	42
3[c]	Synthetic rubber	5
4	RRIM600	93
5	Tjir 1	57
6	PB48	46
7	PR107	69

[a]96% of the calculated epoxidation level.
[b]Same rubber as in No. 1 before epoxidation.
[c]Synthetic polyisoprene, Nutsyn rubber, containing an amino type of antioxidant which could interfere with the HBr titration.

$$
\begin{array}{c}
\text{CH}_3 \\
| \\
-\text{CH}_2-\text{CH}-\text{C}-\text{CH}_2- \\
\diagup \quad | \\
\text{RN} \quad\ \text{OH} \qquad \text{(II)} \\
\diagdown \quad \text{OH} \\
\diagup \\
-\text{CH}_2-\text{CH}-\text{C}-\text{CH}_2- \\
\diagdown \\
\text{CH}_3
\end{array}
$$
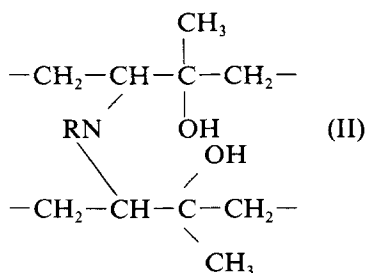
Both mono- and bifunctional amines at low concentrations are able to cause crosslinking, while at higher concentrations they would ring-open all the epoxide groups, forming predominantly structures such as (I), and inhibit the formation of crosslinks. Dehydration under low humidity conditions in dry rubber is represented as follow:

$$
\begin{array}{c}
\text{CH}_3 \\
| \\
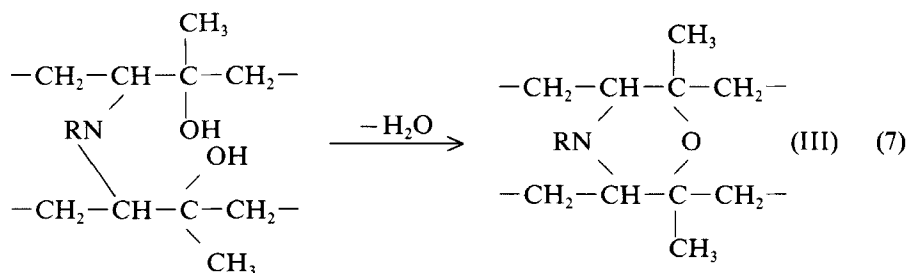-\text{CH}_2-\text{CH}-\text{C}-\text{CH}_2- \\
\diagup \quad | \\
\text{RN} \quad\ \text{OH} \\
\diagdown \quad \text{OH} \\
\diagup \\
-\text{CH}_2-\text{CH}-\text{C}-\text{CH}_2- \\
\diagdown \\
\text{CH}_3
\end{array}
\quad\xrightarrow{\ -\text{H}_2\text{O}\ }\quad
\begin{array}{c}
\text{CH}_3 \\
| \\
-\text{CH}_2-\text{CH}-\text{C}-\text{CH}_2- \\
\diagup \quad \diagdown \\
\text{RN} \qquad \text{O} \qquad \text{(III)} \quad (7) \\
\diagdown \quad \diagup \\
-\text{CH}_2-\text{CH}-\text{C}-\text{CH}_2- \\
| \\
\text{CH}_3
\end{array}
$$

Furthermore, the epoxide hypothesis can accommodate the previously unexplained observation that conditions of low pH during coagulation of latex reduce the extent of crosslinking on storage. The epoxide groups are ring-opened under acidic conditions to diols that have no crosslinking ability.
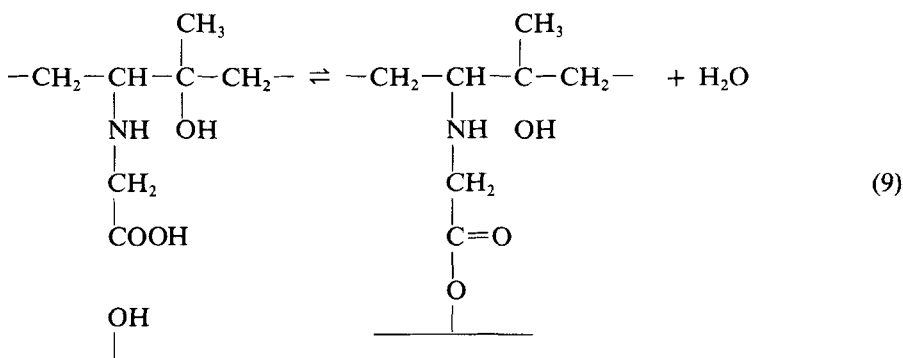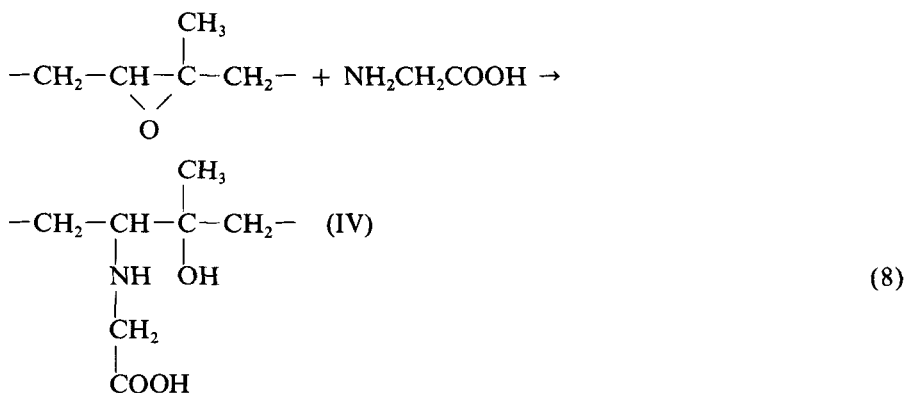
An apparent weakness of the proposal is that it does not adequately explain the accelerating effect of dehydration on the crosslinking reactions. Formation of a structure such as (III) as represented in Eq. (7) should not contribute to more effective crosslinks. In actual fact, studies of the reactions of model compounds have demonstrated that tri-substituted epoxide compounds do not react readily with amine under ambient conditions [12]. Subramaniam and Wong confirmed that the epoxide groups in epoxidized natural rubber did not enhance storage hardening [13].

ROLES OF AMINO ACIDS

The presence of epoxide groups in natural rubber was indirectly shown by the degradation of acid-hydrolyzed rubber with $Pb(OAc)_4$ [14]. Direct evidence came from the NMR studies [15]. Reactions of model compounds show that water or β-substituted hydroxyl group could activate the ring-opening of tri-substituted epoxide to occur smoothly at ambient temperatures. In particular, the model tri-substituted epoxide, similar to rubber epoxide, reacts readily with amino acids in the presence of water [12].

It is conceivable that the epoxide groups can be ring opened by amino acids at the latex stage to give a functionalized rubber with short carboxylic side-chains such

as (IV) below. Crosslinks could subsequently form under low humidity conditions by condensation reactions involving (IV) such as in Eq. (9).

$$
\begin{array}{c}
\underset{\displaystyle \text{O}}{-CH_2-CH-\overset{\displaystyle CH_3}{\underset{\diagdown\ \diagup}{C}}-CH_2-} \ +\ NH_2CH_2COOH \ \rightarrow \\[4mm]
-CH_2-CH-\overset{\displaystyle CH_3}{\underset{\displaystyle NH}{\underset{\displaystyle CH_2}{C}}}-CH_2- \quad (IV) \\
\end{array}
$$

$$
-CH_2-CH-\underset{NH\ \ OH}{C}-CH_2- \quad (IV) \tag{8}
$$

with side chain:
NH OH
|
CH$_2$
|
COOH

$$
\begin{array}{c}
-CH_2-CH-\overset{CH_3}{\underset{\substack{NH\ \ OH \\ | \\ CH_2 \\ | \\ COOH \\ | \\ OH}}{C}}-CH_2- \ \rightleftharpoons \ -CH_2-CH-\overset{CH_3}{\underset{\substack{NH\ \ OH \\ | \\ CH_2 \\ | \\ C=O \\ | \\ O}}{C}}-CH_2- \ +\ H_2O
\end{array} \tag{9}
$$

Such a reaction is favored by the removal of water and is consistent with the observation that the rate of hardening of dry rubber is enhanced by reducing the humidity of the storage environment, e.g., the use of drying agent or high vacuum conditions. In addition, the ester linkage could provide an answer to the previously unexplained observation that storage hardening can be reversed by conditions of high humidity.

Feasibility for Reaction (8) was provided by radiotracer studies which showed that labeled glycine added to fresh latices was incorporated into the rubber at levels close to the known epoxy content [4, 16], as summarized in Table 2.

Strong evidence of the role of amino acids in storage hardening was provided by Gregory and Tan [17] who reported that purified rubber from ultracentrifuged latex did not undergo storage hardening. When the bottom fraction of centrifuged latex was added back to the purified rubber latex, the hardening increased with the concentration of the fraction up to a limiting value. A similar effect was observed when amino acids were added to the purified latex. However, they proposed a modified mechanism involving aldehyde groups with the amino acids as follows:
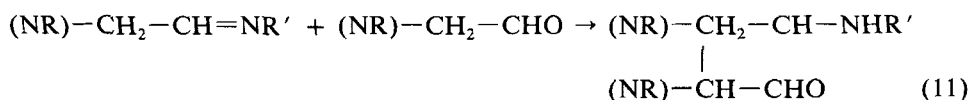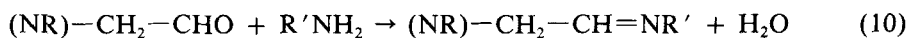
$$
(NR)-CH_2-CHO + R'NH_2 \rightarrow (NR)-CH_2-CH=NR' + H_2O \tag{10}
$$

$$
(NR)-CH_2-CH=NR' + (NR)-CH_2-CHO \rightarrow (NR)-CH_2-\underset{\substack{| \\ (NR)-CH-CHO}}{CH-NHR'} \tag{11}
$$

TABLE 2.   Comparison of Radioactive Glycine Incorporation with
Results of Other Workers

| Clone	Aldehyde[a] groups, mmol/kg	Aldehyde[b] groups, mmol/kg	Epoxide groups, mmol/kg	Radioactive glycine incorporated, mmol/kg
PB5/15	—	1.6	42	29
PB48	—	—	46	30
RRIM501	18	5.4	57	35
PR107	—	3.7	69	44
RRIM600	—	3.7	93	89

[a]Data of Sekhar [6] from inhibition of storage hardening by amine.
[b]Data of Subramaniam [13] by 2,4-dinitrophenylhydrozine method.

where $R'NH_2$ represents the conjugate base of an amino acid. They also speculated that the carboxylate group of the amino acid might participate in the following reaction:

$$(NR)-CH_2-CHO + RCOO^- \rightarrow (NR)-CH-\overline{C}HO + RCOOH \qquad (12)$$
$$\text{nucleophile}$$
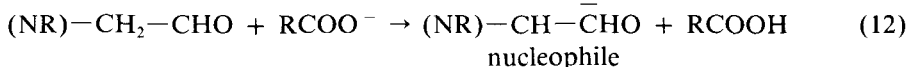
However, this scheme cannot adequately accommodate all their own observations. For example, the cyclic amino acid proline, which they reported to have accelerated storage hardening, could not be involved in imine formation as required by Eq. (10). The structure of proline is
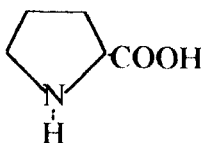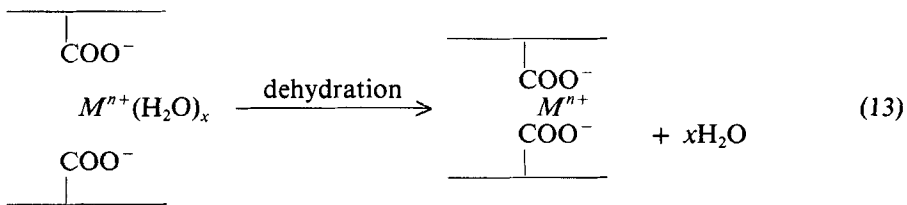

IONIC CROSSLINKING

Another possibility is the formation of ionic crosslinks. Thus the carboxylic groups in rubber, such as Structure (IV), could react with metal ions to form a carboxylate ion.
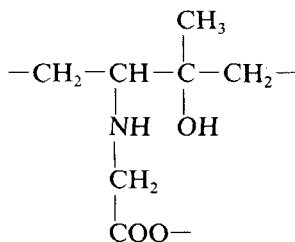
The carboxylate groups may play a role in ionic crosslinking [18]. It has been

reported that the tensile strength of CaO crosslinked carboxylate rubbers was dramatically increased under conditions of low humidity [19]. The formation of ionic crosslinks can be envisaged with links bridged by metals cations, as represented below:

$$
\begin{array}{c}
\overline{\left| \begin{array}{c} \text{COO}^- \end{array} \right.} \\
M^{n+}(H_2O)_x \quad \xrightarrow{\text{dehydration}} \\
\text{COO}^- \\
\overline{\left| \right.}
\end{array}
\qquad
\begin{array}{c}
\overline{\left| \begin{array}{c} \text{COO}^- \\ M^{n+} \\ \text{COO}^- \end{array} \right.} \quad + \ xH_2O
\end{array}
\qquad (13)
$$

The sensitivity to moisture can be readily explained since hydration of the ions would reduce the strength of the link. Conversely, drying the rubber reduces the solvation by water, intensifies the ionic interactions, and hence effectively increases the hardness.

The formation of ionic crosslinks presupposes the presence of suitable linking cations. Fresh latex is known to contain 0.3–0.4% metal ions [20]. Removal of these ions by dialysis is reported to reduce hardening of rubber [18]. Trace metal analysis showed that the process of dialysis decreased the metal content of the rubber sample. However, these results are not conclusive since amino acids, which have also been implicated in the storage hardening, could also be removed by dialysis. Studies of the reversal of the storage hardening process by moisture [2, 4] and polar solvents such as dimethylformamide (DMF) appear to agree with the concept of ionic crosslinks [18].

In our recent work excess Na^+ and K^+ were added to latex before the rubber was isolated [21]. Although the initial pH was adjusted to 8.1, hydrolysis of proteineous materials occurred over 24 hours, resulting in the drop of pH to around 5.8. The results, summarized in Table 3, show that the storage hardening behavior

TABLE 3. Effect of Some Monovalent Cations, Na^+ and K^+, on Storage Hardening of Natural Rubber [21][a]

Metal salt added	Final pH	P_0	P_H	ΔP
Control	5.81	30.1	87.1	57.0
NaNO_3	5.75	29.3	85.6	56.3
KNO_3	5.84	27.9	85.8	57.9

[a]Latex concentration expressed as dry rubber content = 35 $g \cdot dm^{-3}$, [metal salt] = 0.04 M, initial pH 8.1 adjusted by adding dilute NaOH and acetic acid solutions, reaction time = 24 hours, temperature = 40°C. P_0 = initial plasticity of the isolated rubber, P_H = plasticity of the dry rubber after accelerated storage hardening test at 60°C for 24 hours.

of the final rubber is not affected by these monovalent cations. This observation shows that the "swamping effect" [18] of monovalent metal ions on ionic crosslinks does not occur.

The latex was then treated with excess Mg^{2+}, Ca^{2+}, and Ba^{2+} for a specific time before the rubber was isolated, and the storage hardening property was measured. The result is summarized in Table 4.

In comparison to the control sample, Mg^{2+} ion has very small effect on the plasticities of the resulting rubber, while Ba^{2+} has reduced the extent of storage hardening and Ca^{2+} ions inhibit storage hardening. Note that the nitrogen content of the dry rubber (% N) decreases with the pH of the latex prior to the isolation of rubber from the latex. The postulates of ionic crosslinking could not be used to explain the change of % N in the rubber.

These ions are probably involved in the formation of metallic soaps which displace the proteins and free amino acids from the surfaces of the rubber particles in the latex, reducing the incorporation of these compounds into the rubber chains via their reactions with epoxide groups. Consequently, storage hardening is reduced. Thus the most important factor in the storage hardening of natural rubber lies in the amount of incorporated amino acids (as reflected by the nitrogen content). As in the case of purified latex, there is no storage hardening of the rubber.
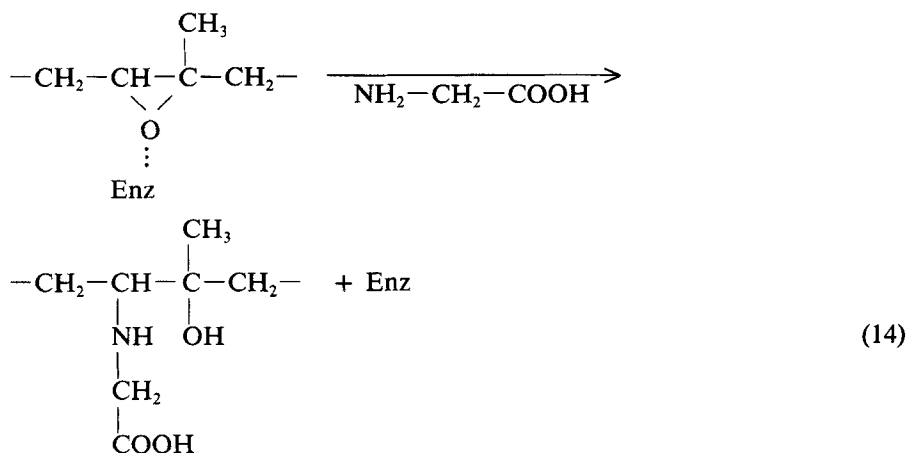
POSSIBLE INVOLVEMENT OF ENZYMES

It has been suggested by Hanzlik and Hilbert [23] that the ring opening of epoxide could be assisted by enzymes. If enzymes are involved, the reaction between amino acids and rubber epoxide might be represented by

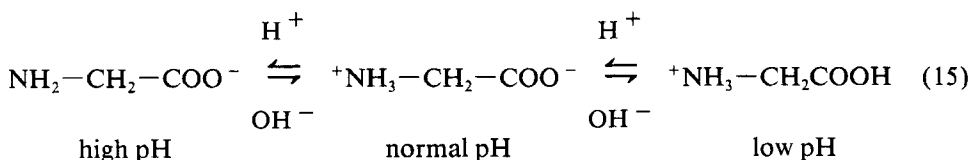TABLE 4. Effect of Mg^{2+}, Ca^{2+}, and Ba^{2+} on Storage Hardening of Natural Rubber [21]

Metal salt added	Final pH	P_0	P_H	ΔP	% N
Purified latex	8.0	24	30	6	0.07
Control	5.5	30	90	60	0.32
$MgSO_4 \cdot 7H_2O$	5.6	30	86	56	0.32
$CaCl_2$	5.7	32	46	13	0.18
$BaCl_2 \cdot 2H_2O$	5.7	31	70	39	0.24

Latex concentration expressed as dry rubber content = 35 $g \cdot dm^{-3}$, [metal salt] = 0.04 M, initial pH 8.1 adjusted by adding dilute NaOH and acetic acid solutions, reaction time = 24 hours, temperature = 40°C. P_0 = initial plasticity of the isolated rubber, P_H = plasticity of the dry rubber after accelerated storage hardening test at 60°C for 24 hours. Purified latex prepared by a procedure described elsewhere [22]. % N = nitrogen content of rubber, determined by a procedure described elsewhere [22]. Control: latex at same rubber concentration without metal salt, left for 24 hours at 40°C before isolating the rubber.

$$
\begin{array}{c}
\overset{\displaystyle CH_3}{\underset{\diagdown \diagup}{-CH_2-CH-\overset{|}{C}-CH_2-}} \\
O \\
\vdots \\
Enz
\end{array}
\quad \xrightarrow{\ NH_2-CH_2-COOH\ }
$$

$$
\begin{array}{c}
\overset{\displaystyle CH_3}{-CH_2-CH-\overset{|}{\underset{|}{C}}-CH_2-} \quad + \ Enz \\
\underset{|}{NH} \quad OH \\
CH_2 \\
| \\
COOH
\end{array}
\qquad\qquad (14)
$$

Generally, enzyme can be deactivated at high temperatures ($>50^\circ$C). Eng [24] has shown that the amount of radioactive glycine incorporation into natural rubber could be reduced to near zero at 60°C. The incorporation of glycine into rubber has also been shown to be pH sensitive [19]. The reaction is not favored at extreme pHs, and the optimum pH is found to be around 8.0.

At low pH the amino group is protonated:

$$
NH_2-CH_2-COO^- \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \ ^+NH_3-CH_2-COO^- \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \ ^+NH_3-CH_2COOH \quad (15)
$$

$$
\text{high pH} \qquad\qquad \text{normal pH} \qquad\qquad \text{low pH}
$$

The protonated amino group is not nucleophilic and thus becomes less reactive toward rubber epoxide. On the other hand, extremely high pH would catalyze the ring opening of epoxide to a diol [12] that is not reactive to amino acids.

CONCLUSION

Any mechanism proposed to explain the storage hardening of rubber should be able to account for the important characteristics of storage hardening that have been identified. These include: 1) the process is accelerated at conditions of low humidity and is reversible by moisture, 2) amines inhibit the hardening if added in sufficient quantity to the latex before isolation of the rubber, 3) removal of protein and amino acids from the latex reduces the extent of hardening, and 4) hardening increases with addition of amino acids.

The closest mechanism at the moment appears to involve the amino acids which are incorporated into the rubber by reaction with the rubber epoxide groups, largely at the latex stage. During the storage of dry rubber, the carboxylate end of the incorporated amino acid could then be involved in the formation of ester or amide linkages, favored by conditions of low humidities, and the crosslinks could be reversed by hydrolysis under conditions of high humidities.

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