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Storage Hardening of Natural Rubber
I. Effect of Epoxide Groups

A. SUBRAMANIAM* AND WONG WAI SUIN**

A small number of epoxide groups were introduced onto purified natural rubber and synthetic cis-*1,4-polyisoprene by reacting the rubbers with* m-*chloroperbenzoic acid. The rubbers were then subjected to the conditions of the accelerated storage hardening test in the presence of an amino acid (glycine). Results showed that epoxide groups made no contribution to storage hardening and are therefore not responsible for storage hardening of natural rubber.*

When natural rubber is stored at room temperature, it tends to harden, *i.e.* its viscosity increases. This phenomenon of storage hardening can be inhibited almost completely by reacting the rubber with hydroxylamine or its salts during production, as in the case of constant viscosity or CV rubber. While the technological problem has been solved, the actual reason for storage hardening is still not fully understood.

Three hypotheses have been put forward to explain storage hardening. In the first hypothesis[1-4], it is suggested that a small number of carbonyl groups — probably aldehydic — are present on the rubber molecule and that these crosslink with the amino acids and proteins present in the non-rubber fraction. In the second hypothesis[5], it is suggested that storage hardening is due to epoxide groups in natural rubber while the third hypothesis[6] considers the functional groups to be ester groups.

One method of resolving the problem is to actually introduce a small number of these functional groups onto the *cis*-1,4-polyisoprene molecule and study whether the product will show the same behaviour as natural rubber under conditions favourable for storage hardening. The introduction of epoxide groups onto *cis*-1,4-polyisoprene is relatively easy.

The work reported here involves the introduction of a small number of epoxide groups onto synthetic *cis*-1,4-polyisoprene and purified natural rubber and the determination of their degree of storage hardening.

EXPERIMENTAL

Preparation of Epoxidised Synthetic *cis*-1,4-polyisoprene

A sample of synthetic *cis*-1,4-polyisoprene (150 g) with a high *cis* content [Ameripol (Goodrich) or Natsyn 2200 (Goodyear)] was dissolved with constant shaking and stirring in toluene (3 litres) to give a 5% (weight/volume) solution. To this was added *m*-chloroperbenzoic acid (1.5 g to 13.5 g, depending on the level of epoxidation required) dissolved in a minimum volume of toluene. The reaction mixture was stirred with a magnetic stirrer for 4 h and the epoxidised rubber was precipitated from solution by pouring into an equal volume of methanol. The rubber thus collected was washed well with methanol and dried under reduced pressure.

Preparation of Purified Natural Rubber

Fresh latex was ultracentrifuged at 50 000 g for 1 h. The cream fraction was collected and dispersed in a solution containing sodium dodecyl sulphate (1% by weight on dry rubber content). The dispersion was filtered through muslin cloth and diluted to the original volume of fresh latex used before being ultra-

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* Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia
** Universiti Sains Malaysia, Minden, Pulau Pinang, Malaysia

centrifuged again for half an hour. The cream was then dispersed in water and recentrifuged and this procedure was repeated once more.

The final purified rubber latex dispersion was precipitated in ethanol and the rubber was extracted with hot ethanol for 16 h under nitrogen. After drying in vacuum, the rubber was left to stand in an excess of *n*-hexane without agitation. After two days, the solution was carefully poured out and dried by filming. More hexane was added to the rubber and the procedure was repeated several times until most of the rubber had gone into solution.

By this procedure, a highly purified gel-free natural rubber sample was obtained.

Preparation of Epoxidised Purified Natural Rubber

The purified natural rubber collected above was epoxidised as described above for synthetic *cis*-1,4-polyisoprene, except for the following changes:

- A lower quantity (10–20 g) of rubber was used for each preparation, with the concentration of *m*-chloroperbenzoic acid adjusted accordingly.
- The concentration of the rubber solution was 2.5% (weight/volume).
- The solution was left to epoxidise overnight.

Chemical Determination of Epoxide Content

The level of epoxidation in the rubber was determined by titration using both the method described in the British Standards[7] as well as the method of Durbetaki[8] which was used by Burfield[9] and Lee[10].

Determination of Storage Hardening

A weighed amount of glycine was dissolved in the minimum amount of water (a few drops) and the solution was dispersed in 20 ml of toluene containing 2 mg of antioxidant (Antioxidant 2246). Epoxidised *cis*-1,4-polyisoprene or purified natural rubber (10 g) was cut into small pieces and added to the toluene with vigorous shaking. The rubber quickly absorbed the solvent. The swollen rubber was stirred thoroughly to disperse the glycine. The swollen rubber was then pressed into a thin film, dried in air and finally in vacuum to remove the solvent. The dry rubber was passed six times through the narrow gap of a two-roll mill. Traces of glycine left in the container were added back to the rubber at this stage. Several Wallace pallets cut from the rubber sheet were heated for 24 h at 60°C over phosphorous pentoxide in vacuum. The test was similar to the accelerated storage hardening test for natural rubber (ASHT) except that it was done in vacuum. The Wallace plasticity values were measured before (P_O) and after (P_H) heating. The difference ($\Delta P = P_H - P_O$) was taken as the extent of hardening.

RESULTS AND DISCUSSION

The epoxidation of olefinic compounds by *m*-chloroperbenzoic acid is known to take place readily at or below room temperature with efficiencies greater than 90%. The theoretical values for the level of epoxidation calculated from the amount of *m*-chloroperbenzoic acid added are shown in *Table 1.* As mentioned in an earlier paper[11], the determination of epoxide groups by titration (both the British Standard and Durbetaki methods) gave values much lower than the theoretical values. These values measured by the British Standard method are shown in *Table 1* for both *cis*-1, 4-polyisoprene and purified natural rubber.

Based on the number average molecular weight, $\overline{M}n$, of 300 000 for the rubbers the theoretical levels of epoxidation are equivalent to 17, 52, 105 and 157 epoxide groups per molecule at concentrations of *m*-chloroperbenzoic acid of 10, 30, 60 and 90 mg per gramme, respectively. For *cis*-1,4-polyisoprene, the measured values are equivalent to 13, 40, 75 and 110 groups per molecule and for purified natural rubber, 8, 12, 57 and 101 groups per molecule, respectively.

Burfield and Gan[12] have reported that the level of epoxide groups naturally present in different clonal rubbers range from 46 to 111. Thus the number of epoxide groups introduced

TABLE 1. CALCULATED AND MEASURED VALUES OF EPOXIDATION LEVEL

Concentration of m-chloroperbenzoic acid (mg/g rubber)	Calculated value of epoxide content (mole per cent)	Measured value (mole per cent) Polyisoprene	Measured value (mole per cent) Purified natural rubber
10	0.39	0.3	0.18
30	1.18	0.9	0.27
60	2.37	1.7	1.3
90	3.55	2.5	2.3

into *cis*-1,4-polyisoprene in the present experiments is not dissimilar to the number of epoxide groups reported in NR. Therefore the discrepancy between the measured and calculated values is not important in the discussion of the storage hardening results.

The present experiments are based on the fact that highly purified natural rubber does not undergo storage hardening on its own. However, when an amino acid like glycine is incorporated into the purified rubber, the rubber hardens in the accelerated storage hardening test, just like unpurified natural rubber.

Epoxidised synthetic *cis*-1,4-polyisoprene when reacted with glycine in increasing concentrations and subjected to the accelerated storage hardening test, showed no hardening *(Table 2)*. The epoxidised synthetic *cis*-1,4-polyisoprene behaved exactly as the unepoxidised sample, thus indicating that the epoxide groups did not respond to the accelerated storage hardening test even in the presence of an amino acid.

The P_O and P_H values given in the tables are the averages of three readings. Assuming an error of ±1 unit per reading, ΔP is expected to have a maximum error of 2 units. Many of the readings in *Table 2* show a negative value for ΔP. This could be expected if traces of *m*-chlorobenzoic acid (product of the epoxidation reaction) left in the rubber caused some oxidation of the rubber, despite the presence of antioxidant.

The results for unepoxidised and epoxidised purified natural rubber are given in *Table 3*. The unepoxidised or epoxidised purified natural rubber showed negligible hardening in the absence of glycine. The small value of ΔP shown could be due to other side reactions but this is small compared to the increase shown in the presence of glycine. In the presence of increasing concentrations of glycine, both unepoxidised and epoxidised purified natural rubber showed considerable hardening (P_H/P_O values were 2 or higher). The epoxidised purified natural rubber actually showed a lower hardening than the unepoxidised purified natural rubber. These results clearly show that the epoxide groups introduced did not contribute to storage hardening.

The lower degree of hardening seen in the epoxidised purified natural rubber could arise, for example, if some of the glycine molecules reacted with the epoxide groups and were therefore not available for storage hardening. Another possibility is that small amounts of epoxide groups could cause storage hardening but large amounts could disturb this reaction. However, the fact that the number of epoxide groups introduced into *cis*-1,4-polyisoprene was similar to the number of epoxide groups found in NR[12], would tend to lessen this possibility.

It is also possible that epoxide groups alone are not sufficient for storage hardening but that some other functional groups in NR are also required for the reaction. However this seems unlikely in view of the fact that epoxidised

TABLE 2. STORAGE HARDENING OF EPOXIDISED SYNTHETIC CIS-1,4-POLYISOPRENE

Concentration of m-chloroperbenzoic acid used (mg/g rubber)	Concentration of glycine (mg/g rubber)	Wallace plasticity, P_O	Wallace plasticity after hardening, P_H	Extent of hardening, ΔP
0[a]	0	44	44	0
	1	42	43	1
	3	40	41	1
	5	41	41	0
	10	41	42	1
10	0	46	37	-9
	1	44	41	-3
	2	45	41	-4
	5	40	37	-3
30	0	43	41	-2
	1	45	44	-1
	2	44	43	-1
	3	42	42	0
	5	44	44	0
	10	44	43	-1
60	0	45	37	-8
	3	43	40	-3
	5	41	38	-3
	10	42	40	-2
90	0	45	37	-8
	3	42	39	-3
	5	40	38	-2

[a] Control — treated like the epoxidised samples except that no m-chloroperbenzoic acid added.

TABLE 3. STORAGE HARDENING OF EPOXIDISED PURIFIED NATURAL RUBBER

Concentration of m-chloroperbenzoic acid used (mg/g rubber)	Concentration of glycine (mg/g rubber)	Wallace plasticity, P_O	Wallace plasticity after hardening, P_H	Extent of hardening, ΔP
0[a]	0	39	42	3
	1	41	74	33
	3	43	87	44
	5	41	86	45
	10	42	86	44
10	0	40	39	- 1
	1	40	62	22
	2	40	70	30
	5	41	85	44
30	0	40	43	3
	1	41	58	17
	2	41	70	29
	5	40	76	36
	10	42	89	47
60	0	41	43	2
	3	42	62	20
	5	46	79	33
	10	45	87	42
90	0	42	47	5
	3	39	52	13
	5	45	84	39
	10	45	87	42
	20	42	88	46

[a] Control

purified natural rubber did not show a higher degree of storage hardening than the unepoxidised sample in the present experiments.

The maximum hardening of the unepoxidised purified natural rubber was observed at a concentration of glycine higher than 27 × 10^{-3} mole per kilogramme rubber. The concentration of glycine required to give maximum hardening was earlier reported[4] to be 2 × 10^{-3} to 6 × 10^{-3} mole per kilogramme rubber. This discrepancy could be due to two reasons. The purified rubber in the earlier experiments was not as pure as in the present work. The glycine was added to the dry rubber in the present work and the homogeneity of mixing would not be as good as the addition in the latex stage as in the earlier work.

The results given in *Tables 2* and *3* were generally true whether the antioxidant was present or not. In the absence of antioxidant, the samples sometimes showed a sticky appearance and reduced P_H values, probably due to oxidation. This was also the reason for carrying out the test in vacuum. Samples hardened in air over phosphorus pentoxide showed lower P_H values.

Since the work was completed, natural rubber samples with much higher epoxidation levels *viz.* 10, 25 and 50 mole per cent have become available. Experiments with these rubbers showed that in the presence of glycine, these rubbers actually hardened less than the control unepoxidised rubber under the conditions used in the accelerated storage hardening test.

From all the above results it is clear that epoxide groups in synthetic polyisoprene or natural rubber do not contribute to storage hardening. It can thus be concluded that, while epoxide groups may be present in natural rubber, they are not responsible for storage hardening.

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