

Contribution of Storage Hardening to Plasticity Retention Index Test for Natural Rubber

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Two experiments were designed to investigate the influence of natural or storage hardening on Plasticity Retention Index (PRI) test results. The first experiment involved ageing of PRI test-pieces under vacuum and the second made use of sequential hardening and ageing of the rubber. Results from both experiments showed that storage hardening had a marked effect on PRI test results, even for natural rubber samples which were not freshly prepared. Quantitative estimates of the contribution of hardening to the PRI test were correlated with accelerated storage hardening test results. The correlation indicated that approximately half of the total potential of a rubber sample for storage hardening occurs during the PRI ageing treatment.

The Plasticity Retention Index (PRI) is a measure of the susceptibility of raw rubber to thermal oxidative degradation. It is determined by measuring the Wallace plasticity of a rubber sample before and after ageing for 30 min in an air oven at 140°C. Since its inclusion in the Standard Malaysian Rubber (SMR) specifications, it has become one of the primary indicators of raw rubber quality for Technically Specified Rubbers.

The phenomenon of storage or natural hardening in raw rubber has also been known for many years. It is the slow increase in viscosity of rubber, which occurs during transport and storage and is thought to be due to the linking of oxygen-containing groups on the NR polymer. Most of the reported evidence is consistent with the groups being aldehydic in nature^{1,3}, but the involvement of rubber-bound epoxide groups has also been postulated^{4,6}. The hardening process certainly involves amino-acids which are present in natural rubber^{2,7}, though the mechanism of their involvement has been the subject of some debate^{5,8}. Whatever the nature of the chemical reactions responsible for storage hardening, they can be effectively and economically inhibited by the addition of chemicals such as hydroxylamine to the rubber⁹. However, while a number of viscosity-

stabilised grades of NR are well established, the majority of rubber produced is still not protected against this natural hardening process.

In spite of the fact that storage hardening is known to be accelerated by increased temperature and by conditions which favour removal of water from the rubber¹⁰, the influence of hardening on PRI test results has not been properly assessed. It has been shown that the contribution of storage hardening to oven ageing gives artificially high PRI values for freshly-prepared rubber samples^{3,11,12}. PRI results in excess of 100, indicating a net increase in Wallace plasticity on ageing, have been reported for some of these samples. The SMR specifications for PRI, which are generally 10 units higher for the producers than for the consumers, reflect the general acceptance that storage hardening does influence PRI results in freshly-prepared natural rubber. It is not clear from the literature however, whether the above effect is of significance in commercial samples of NR or rubber that has been stored for some time. In a series of papers on the kinetics of degradation during the PRI test, the contribution of storage hardening was assumed to be negligible without sufficient justification^{11,13}. An attempt is made here to investigate, both qualitatively and quantitatively,

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the influence of storage hardening on PRI test results from various grades of Malaysian natural rubber of various ages.

MATERIALS AND METHODS

Fresh latex rubber was prepared by coagulating fresh field latex with formic acid at pH 4.5, passing the coagulum five times through a creping mill and drying the creped sheet at 100°C until just dry by visual inspection (1.5–2 h). Testing was carried out within 24 h of the latex being collected from the trees. Other samples of natural rubber were taken from stocks which had been stored under various ambient conditions.

All plasticity tests were carried out on one Wallace Rapid Plastimeter for which operating conditions and sample preparation procedures conformed to requirements for SMR testing¹⁴. Three test pellets were used for each test and the result quoted is the median. The pellets were treated in one of the following ways before testing the Wallace plasticity:

- P_o – No treatment
- P_{30} – Aged for 30 min at 140°C in an air oven, then allowed to cool
- P_H – Placed in a vacuum desiccator over phosphorus pentoxide, evacuated for 1 h, stored for 48 h at 60°C under vacuum then cooled over 1 h
- P_{30+H} – Aged as for P_{30} then treated as for P_H
- P_{H+30} – Treated as for P_H then aged as for P_{30}
- P_S – Placed on the base of a preheated vacuum desiccator which was then evacuated for 3 min before sealing and heating at 140°C for 30 min. The desiccator was cooled for 3 min then opened and the rubber pellets removed to cool in air.

RESULTS AND DISCUSSION

Anaerobic Ageing

To probe experimentally the subject of this paper, the most direct approach was considered to be to carry out the ageing process of the PRI test in the absence of air. Unfortunately, this approach was complicated by two matters. Firstly, the experimental inaccuracies were expected to be large because the application of vacuum necessitated the use of a closed container of considerable mass. The temperature – time profile of the rubber samples could not therefore be controlled with the same accuracy as for those aged in an air oven. Secondly, even in the absence of air, thermal oxidative degradation could not be completely eliminated because of dissolved oxygen in the rubber and the contribution of anaerobic thermal degradation. For this reason, the results of the P_S test which is comparable to a P_{30} test in the absence of air (*Table 1*) do not provide a measure of the contribution of hardening to PRI, but rather a combination of hardening and thermal degradation. To obtain realistic estimates of the contribution of hardening, it was necessary to obtain independent information on the degree of thermal degradation for each rubber sample. This was achieved by hardening a sheet of the rubber to its full extent using the accelerated method (P_2O_5 /vacuum/60°C/48 h), then re-testing P_o and P_S .

The overall PRI ageing process can be considered as the sum of three contributions which are assumed to be mutually independent:

- A – the contribution of oxidative degradation
- T – the effect of thermal degradation which is taken to include the contribution from dissolved oxygen
- H – the effect of natural hardening

If A , T and H are defined as the respective changes in plasticity as a percentage of P_o and S is defined as $\frac{P_S - P_o}{P_o} \times 100$ then,

TABLE 1. WALLACE PLASTICITY DATA FOR AEROBIC AND ANAEROBIC AGEING OF VARIOUS NATURAL RUBBER SAMPLES AT 140°C

Sample	P _O (W.P. units)	P ₃₀ (W.P. units)	P _S (W.P. units)	PRI (% of P _O)	S (% of P _O)
A1	38	40	50	107	+ 32
A1Hd	80	52	71	65	- 11
A2	51	46	57	90	+ 12
A2Hd	95	53	63	56	- 34
A3	59	44	65	74	+ 9
A3Hd	86	51	78	60	- 10
B1	45	39	54	86	+ 19
B1Hd	72	46	64	64	- 11
B2	56	28	40	50	- 29
B2hd	68	26	41	39	- 40
B3	50	40	52	79	+ 3
B3Hd	65	47	54	72	- 18

A1-A3 are fresh latex rubber samples

B1 is a six-month-old sample of SMR L

B2 is a six-month-old sample of SMR 10

B3 is a nine-year-old sample of RSS 1

The postscript Hd refers to samples which were hardened in vacuum over P₂O₅ at 60°C for 48 h before testing.

$$PRI_{\text{raw}} - 100 = A + T + H \quad \dots 1$$

$$\text{and } S_{\text{raw}} = T + H \quad \dots 2$$

$$\text{likewise, } PRI_{\text{hard}} - 100 = A + T \quad \dots 3$$

$$\text{and } S_{\text{hard}} = T \quad \dots 4$$

where the subscript 'raw' denotes raw rubber values and the subscript 'hard' indicates values for the fully hardened samples. It can be seen that estimates of H are obtainable both by subtraction of Equation 4 from Equation 2 and of Equation 3 from Equation 1.

$$\text{Thus } H = PRI_{\text{raw}} - PRI_{\text{hard}} \quad \dots 5$$

$$\text{and } H = S_{\text{raw}} - S_{\text{hard}} \quad \dots 6$$

There is reasonable agreement between values of H obtained from Equations 5 and 6 (Table 2) considering the experimental limitations and the assumptions made. The average value of H derived for the various rubber samples ranged from 11 to 42. If these

results are converted to absolute changes in Wallace plasticity, h , increases of 6 to 20 units are obtained (Table 2).

Successive Ageing and Hardening

Due to the limitations of the direct approach discussed above, an alternative, indirect probe to the subject of study was considered.

If a certain amount of hardening does occur during the ageing test, then the capacity of a rubber sample for storage hardening would be expected to be lower after ageing than before. Likewise, the softening of the rubber during ageing should be greater for a hardened sample than it was before storage hardening. The tests P_{30+H} and P_{H+30} were designed to examine these differences. For this approach to have quantitative significance, it is necessary for the softening and hardening reactions to be mutually independent. These conditions could not initially be assumed since aldehyde groups are among

TABLE 2. ESTIMATES OF CONTRIBUTION OF STORAGE HARDENING TO PRI AGEING RESULTS

Sample	H _{eq5} (% of P _O)	H _{eq6} (% of P _O)	Mean H (% of P _O)	h (W.P. units)	ΔP (W.P. units)
A1	+42	+43	42.5	16	42
A2	+34	+46	40.0	20	44
A3	+14	+19	16.5	10	27
B1	+22	+30	26.0	12	26
B2	+11	+11	11.0	6	12
B3	+7	+21	14.0	7	15

the products identified from autoxidation of NR and such groups are almost certainly involved in the storage hardening process^{1,2}. Furthermore, the crosslinks or chemical bonds responsible for the hardening phenomenon could be significantly more or less susceptible to oxidative cleavage than the polymer itself.

Various Wallace plasticity measurements for samples of various grades of natural rubber ranging in age from one day to eleven years were made (Table 3). It can be seen that the reduction in Wallace plasticity of the raw rubber ($P_O \rightarrow P_{30}$) is generally less than that for the hardened samples ($P_H \rightarrow P_{H+30}$) whether these are considered as percentage changes or as absolute changes in plasticity. Also, the hardening of aged samples ($P_{30} \rightarrow P_{30+H}$) is less than that for the unaged samples ($P_O \rightarrow P_H$) except in several of the very old samples in which storage hardening was essentially complete. These results provide qualitative support for the hypothesis that natural hardening occurs during the PRI ageing process.

Considering the results in Table 3 quantitatively, it is observed that there is good agreement between the P_{30+H} values and the corresponding P_{H+30} values. A statistical analysis of the figures reveals that P_{30+H} is greater than P_{H+30} by an average of 0.9 units for the thirty-nine samples while the mean difference between the two measurements is 2.3 units. The actual values of P_{H+30} range from 17 to 58 units with a mean of 40 and standard deviation of 10.2 units. It is

conceivable that the good agreement between P_{30+H} and P_{H+30} is the result of two or more opposing influences of the hardening process on oxidisability and *vice versa*. A more convincing explanation, however, is that the two reactions are in fact occurring independently. Thus, the same final plasticity is reached irrespective of the order in which the ageing and hardening occur.

A further implication of the agreement between P_{30+H} and P_{H+30} for the various natural rubber samples is that plasticity changes due to thermal oxidation must be considered in absolute terms rather than as a percentage of P_O when comparing rubber samples of different initial plasticities. The underlying rate of change of plasticity due to thermal oxidation seems to be independent of the initial plasticity. This deduction is in contrast to published reports in which first-order kinetics have been observed^{11,15} and which presumably led to results¹⁵ of standard PRI tests being expressed as a percentage of P_O . In neither of the earlier studies however, was any attempt made to isolate the effects of storage hardening from the oxidative softening process.

By accepting the above explanation and its implications, two equations can be written to obtain values for h , the absolute change in Wallace plasticity due to storage hardening which occurs during the ageing of each sample:

$$h = (P_H - P_{H+30}) - (P_O - P_{30}) \quad \dots 7$$

$$h = (P_H - P_O) - (P_{30+H} - P_{30}) \quad \dots 8$$

TABLE 3. WALLACE PLASTICITY DATA FOR VARIOUS SAMPLES OF NATURAL RUBBER

Sample No	Age	P _O	P ₃₀	P _H	P _{30+H}	P _{H+30}
L/1	1 week	41	37	70	48	56
L/2	1 week	42	39	76	50	56
L/3	1 week	43	39	75	51	57
L/4	1 week	43	39	77	50	51
L/5	1 week	41	36	68	45	46
L/6	1 day	52	48	87	64	58
L/7	1 month	43	37	64	43	45
L/8	1 month	42	35	61	43	44
L/9	1 month	45	39	70	50	50
L/10	1 month	42	35	59	45	45
L/11	1 month	45	40	74	50	50
L/12	6 months	45	39	72	45	46
L/13	2 years	47	39	65	49	48
L/14	9 years	50	25	67	35	35
L/15	9 years	49	27	56	36	34
L/16	9 years	67	40	74	48	46
L/17	9 years	55	31	67	38	35
L/18	9 years	63	36	71	46	42
10/1	1 week	47	34	66	41	42
10/2	1 week	45	33	57	40	40
10/3	1 week	42	31	56	39	38
10/4	1 week	43	31	59	38	37
10/5	1 week	46	32	68	44	40
10/6	1 week	50	36	70	44	40
10/7	1 week	47	35	70	45	42
10/8	1 week	45	29	66	38	37
10/9	1 week	45	32	65	37	36
10/10	1 week	39	23	58	31	28
10/11	6 months	56	28	75	38	34
10/12	11 years	38	24	41	28	25
10/13	9 years	41	16	49	21	20
10/14	9 years	38	20	49	25	23
10/15	9 years	47	22	59	30	26
10/16	9 years	42	19	49	28	24
10/17	9 years	44	17	55	19	17
CV/1	1 day	45	39	58	47	45
CV/2	1 day	45	38	50	43	42
5/1	11 years	42	31	42	34	31
RS/1	11 years	50	40	75	50	49

Age corresponds to approximate time from drying of the raw rubber

Sample codes L/, 10/, CV/, 5/, and RS/ correspond to SMR L, SMR 10, SMR CV, SMR 5 and RSS 1 grades of natural rubber respectively.

Values of h derived using these two equations (Table 4) range from -2 to $+25$ Wallace plasticity units.

Correlation of Estimates with Measured Values of Storage Hardening

The amount of hardening which occurs during the standard PRI ageing, h , has been found to vary widely (Tables 2 and 4). This variation is not surprising in view of the variety of age and consequent variety in potential for storage hardening of the samples. The capacity of each sample for storage hardening is taken as $P_H - P_O$ and is denoted as ΔP . The values of ΔP for the samples studied ranged from 0 to 44 units (Tables 2 and 4). A plot of h against ΔP (Figure 1) shows the correlation between the estimate of the contribution of hardening to PRI and the measured potential of the rubber for natural hardening. Although the points from the anaerobic ageing experiments tend towards a line of lower gradient compared to the other results, there is reasonable agreement between the two experimental approaches. Taking all of the results together, the value of the linear coefficient which is derived will be influenced more by the greater number of data points from the indirect experimental approach. This weighting reflects the greater confidence in the reliability of results from the latter set of experiments. Linear regression analysis gives the best straight-line fit for the points corresponding to the equation:

$$h = 0.59 \Delta P - 1.1$$

with a correlation coefficient of 0.83. Alternatively, the best straight line passing through the origin for the same set of points gives the equation:

$$h = 0.54 \Delta P$$

with a correlation coefficient of 0.82. This degree of correlation is acceptable, considering the level of accuracy of the measurements. In the absence of a satisfactory explanation of the practical significance of an intercept, the latter relationship between h and ΔP seems to be more appropriate.

The importance of the hardening effect on PRI test results can be judged by considering an example. A typical SMR L tested by the producer could be expected to have a P_O of around 40 and ΔP of 25 units while its PRI could be 90%. According to the relationship derived from this work, the contribution of hardening would be about 0.54×25 or 13.5 Wallace plasticity units, which corresponds to 33% of P_O . Thus, the PRI results would be 33 units lower than the one quoted if the hardening effect was absent. A similar exercise for a typical SMR 10 sample with P_O of 45 and ΔP of 15 provides an estimate of eighteen percentage points as the influence of natural hardening on PRI results.

While the effects illustrated by the above examples are large, they do not invalidate the PRI test as a means of comparing raw rubbers of the same grade, as these would generally have similar potentials for storage hardening. The results do indicate however, that PRI test results may be misleading if they are used to compare the oxidisability of different grades of rubber. The test is particularly unsuitable for comparing the resistance to oxidation of stabilised grades with that of unstabilised grades of NR.

CONCLUSIONS

Results from two different sets of experiments have shown that storage hardening does have a significant influence on the change in plasticity which occurs during ageing for the standard PRI test. This influence is evident in all samples of raw natural rubber except those which have little or no potential for storage hardening, either because of viscosity stabilisation or through old age.

Both sets of experiments gave results which indicated an approximately linear correlation between the extent of hardening occurring during PRI ageing, h and ΔP . The overall relationship of $h = 0.54 \Delta P$ with a correlation coefficient of 0.82 is based on all of the results from both sets of experiments. The relationship between h and the measured value ΔP seems to be independent of the grade of NR and its age,

TABLE 4. CALCULATED VALUES OF ABSOLUTE CHANGES IN WALLACE PLASTICITY AND MEASURED VALUES OF ΔP FOR VARIOUS NATURAL RUBBER SAMPLES

Sample No.	h(eq 7)	h (eq 8)	Mean h	ΔP
L/1	10	18	14	29
L/2	17	23	20	34
L/3	14	19	16.5	32
L/4	22	23	22.5	34
L/5	17	18	17.5	27
L/6	25	19	22	35
L/7	13	15	14	21
L/8	10	11	10.5	19
L/9	14	14	14	25
L/10	7	7	7	17
L/11	19	19	19	29
L/12	20	21	20.5	27
L/13	9	8	8.5	18
L/14	7	7	7	17
L/15	0	- 2	- 1	7
L/16	1	- 1	0	7
L/17	8	5	6.5	12
L/18	2	- 2	0	8
10/1	11	12	11.5	19
10/2	5	5	5	12
10/3	7	6	6.5	14
10/4	10	9	9.5	16
10/5	14	10	12	22
10/6	16	12	14	20
10/7	16	13	14.5	23
10/8	13	12	12.5	21
10/9	16	15	15.5	20
10/10	14	11	12.5	19
10/11	11	7	9	19
10/12	2	- 1	0.5	3
10/13	4	3	3.5	8
10/14	8	6	7	11
10/15	8	4	6	12
10/16	2	- 2	0	7
10/17	11	9	10	11
CV/1	7	5	6	13
CV/2	2	1	1.5	5
5/1	0	- 3	- 1.5	0
RS/1	16	15	15.5	25

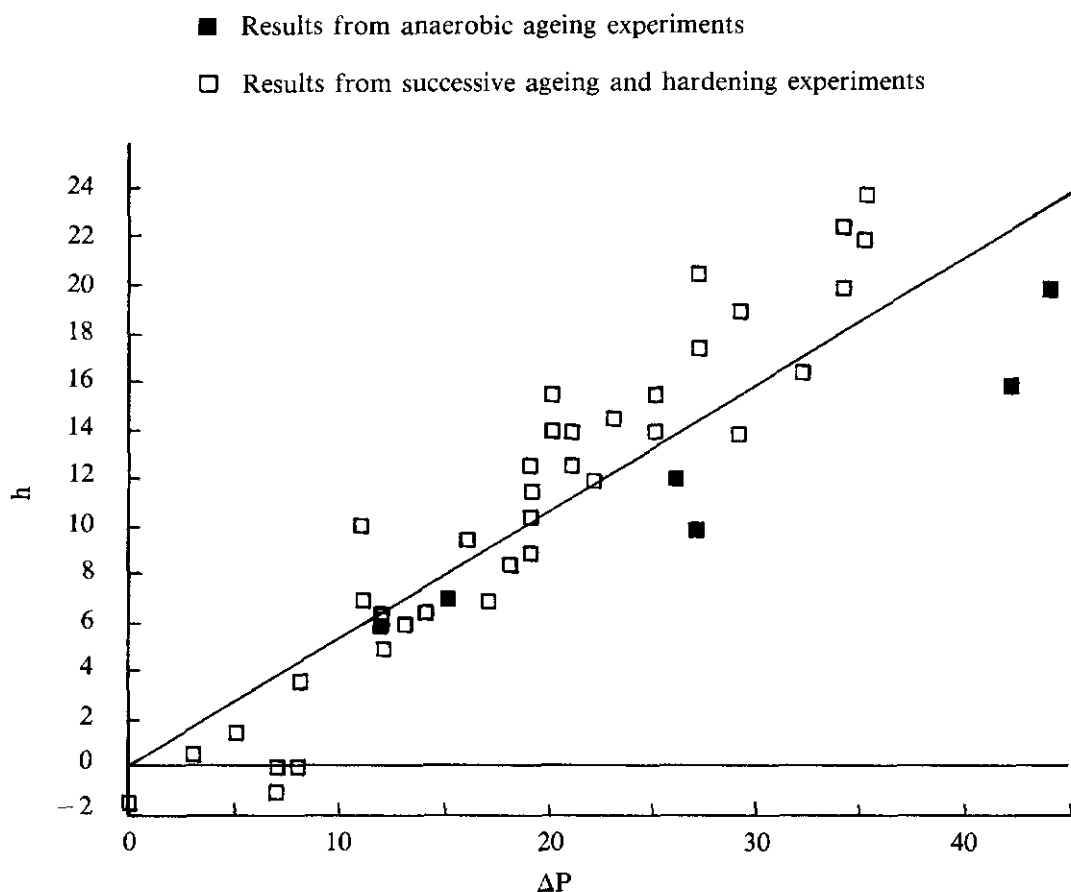


Figure 1. Correlation between values of h derived from two experiments and measured values of ΔP .

so this may be a useful empirical tool for estimating the contribution of hardening to PRI test results.

Freshly-produced CV grades of SMR are known to give PRI values comparable to those of unstabilised grades from the same latex. By definition, natural rubber graded as CV has very limited ability for storage hardening ($\Delta P < 7$). In the light of the findings presented here, it seems that by stabilising the viscosity of natural rubber with hydroxylamine, its susceptibility to thermal oxidative degradation is reduced. This effect is the subject of continuing studies in this laboratory.

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