

EFFECT OF WAREHOUSING ON PROPERTIES OF NATURAL RUBBER SHEETS

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Bales of ribbed smoked sheets (RSS) were stored in warehouses for a period of one year and the changes in the quality parameters of rubber were compared with those stored in an ideal low humidity environment. Sheets were affected by mould within six months of storage while no mould growth was observed for the sheets stored at low humidity. Mooney viscosity, initial plasticity and gel content of the sheets increased while plasticity retention index decreased on storage. These changes were less at low humidity and low temperature. Volatile matter of the sheets increased on storage whereas acetone extractables and strength of the sheets decreased slightly. The physical and ageing properties of vulcanizates were not affected by storage of the RSS.

Key words: Natural rubber, Sheet rubber, Storage, Warehousing.

INTRODUCTION

The major marketable form of natural rubber (NR) in India is Ribbed Smoked Sheets (RSS). The rubber is often stored for varying periods prior to product manufacture. The growers and dealers store rubber anticipating a better price while the manufacturers for ensuring sufficient stock for their production. RSS is also stored during market intervention and bulk procurement by government agencies for price stabilization.

Earlier reports suggest that storage of raw NR could affect some of its properties, the most tangible change being an increase in viscosity referred to as storage hardening (Wood, 1953; Sekhar, 1960; Bristow, 1974). The physical appearance could also be affected adversely by mould growth, stickiness and deformity of the bale. There are no standard specifications for the storage of raw rubber though specifications are available for the storage of vulcanized rubbers and for rubber

products (ISO, 1973; BS, 1963; DIN, 1955).

The major factors that influence the quality of natural rubber during storage are the environmental conditions and the duration of storage. An understanding of the impact of these factors on the rheological and technological aspects of sheet rubber will be beneficial in evolving guidelines for storage of raw rubber. Also, the impact of storage of raw rubber on the technological properties of the resulting vulcanizates has to be understood. In the present work, sheet rubber bales were stored in actual warehouse conditions for a period of one year and the changes in quality parameters of rubber were compared with bales stored in an ideal low humidity environment.

EXPERIMENTAL

Sheet rubber collected from dealers and from the Central Experiment Station of

the Rubber Research Institute of India was used for the study. These were stored as 50 kg bales at three different warehouses of the Kerala State Warehousing Corporation at Mavelikara, Chalakudy and Kottayam up to 12 months after taking a composite sample from each bale to study the initial properties. Composite samples were also drawn periodically after 3, 6 and 12 months of storage and the raw rubber properties and the strength of raw rubber sheets determined. The temperature in the warehouses ranged from 29-38°C and the relative humidity from 70-75 per cent. Another set of sheets was stored in an area of low relative humidity (55-60 %) and low temperature (25±2°C) as control for comparison.

Volatile matter, Mooney viscosity, Wallace plasticity, gel content, plasticity retention Index (PRI) and acetone extractables of the samples were determined periodically as per standard test methods. Breakdown characteristics of the sheets were measured by masticating 250 g of the sample in a Haake rheocord 90 at 60 rpm and at 40°C for 10 minutes. Mastication behavior of the samples was assessed in terms of breakdown index and other associated parameters (Bartha *et al.*, 1983). The following parameters were measured.

TQ₅ : Torque at the fifth minute

TQ₁₀ : Torque at the tenth minute

BI : Rate of breakdown as measured from the drop in torque (TQ₅ - TQ₁₀) with time

TTQ : Totalized torque at tenth minute

ΔT : Difference in temp at 10th minute

Infrared spectrum of the sample was recorded using Shimadzu Fourier Transform Spectrophotometer (DR-8001). Strength of

raw rubber sheets as breaking load was determined in a Zwick Universal Testing Machine (Model 1474) using samples of dimensions 40 x 25 x 3 mm and at a cross-head speed of 50 mm/min.

To assess the effect of storage on processing and technological properties, HAF black filled compounds were prepared in a laboratory model two roll mixing mill. The formulation of the mix is given in Table 1. The cure behaviour of each sample was assessed at 150° C using a Monsanto Rheometer R 100. Test samples were moulded in an electrically heated hydraulic press at 150°C to their respective optimum cure times. Dumb-bell shaped test pieces were punched from the vulcanized tensile sheets along the direction of the grain and the tensile properties assessed as per ASTM D 412-98a (02). Tear strength was determined as per ASTM D 624-00, Hardness (ASTM D2240-03), compression set (ASTM D395-03), heat buildup (ASTM D 623-99, Goodrich Flexometer) and rebound resilience (ASTM D 1054-02, Dunlop Tripsometer) were also determined. Abrasion loss was determined as per DIN 53516-77. Ageing of the vulcanizates was done at 70°C for 7 days (ASTM D 573-99) and the percentage retention of tensile properties were determined.

Table 1. Formulation

Ingredient	Parts by weight
Natural rubber	100.0
Zinc oxide	5.0
Stearic acid	2.0
HAF black	40.0
Naphthenic oil	4.0
CBS*	0.6
S	2.5

* N-Cyclohexylbenzthiazyle solphenamide

RESULTS AND DISCUSSION

The impact of storage on the properties of the sheets and the vulcanizates prepared there from was evaluated.

Volatile matter

The changes in volatile matter during storage are shown in Table 2. Initial volatile matter was observed to be lower for samples stored at ideal conditions. As the storage period increased volatile matter increased significantly for all the samples. This is mostly on account of absorption of moisture from the atmosphere because of the hygroscopic nature of the proteins in rubber.

Mooney viscosity

Table 3 shows the effect of storage on Mooney viscosity. This gives an indication of the mechanical work required to give mixes with consistent rheological properties after compounding of the raw rubber. It was observed that as the storage period is in-

creased, there is significant increase in viscosity of rubber stored in all the locations. Initially, there was a significant variation among the locations. The extent of increase was more for the samples stored in warehouses.

Initial plasticity

The effect of storage period on Initial plasticity is given in Table 4. Initial plasticity (Po) as measured by the Wallace Plastimeter is also an important parameter indicating bulk viscosity. Similar to Mooney viscosity, Po also increased on storage in all the locations and the increase was more for the samples stored in the warehouses.

Gel content

The effect of storage on gel content of the samples is given in Table 5. The increase in gel content was significant for sheets stored at all the locations. Similar to the observations on Mooney viscosity and initial plasticity, increase in gel content was observed

Table 2. Effect of storage on volatile matter (%)

Storage period (Months)	Low humidity area	Mavelikkara	Chalakkudy	Kottayam
0	0.50	0.66	0.60	0.60
3	0.59	0.76	0.70	0.67
6	0.67	0.83	0.76	0.73
12	0.72	0.89	0.80	0.77
VR	**	**	**	**
CD ($P \leq 0.05$)	0.08	0.09	0.08	0.05

Table 3. Effect of storage on Mooney viscosity, ML (1+4) at 100°C

Storage period (Months)	Low humidity area	Mavelikkara	Chalakkudy	Kottayam
0	82	82	83	83
3	83	83	87	86
6	86	86	90	90
12	89	92	96	95
VR	**	**	**	**
CD ($P \leq 0.05$)	2.24	2.7	2.31	2.91

Table 4. Effect of storage on initial plasticity

Storage period (Months)	Low humidity area	Mavelikkara	Chalakkudy	Kottayam
0	46	46	47	48
3	47	49	49	50
6	49	52	52	52
12	53	58	56	56
VR	**	**	**	**
CD ($P \leq 0.05$)	1.75	1.97	1.91	1.89

Table 5. Effect of storage on gel content (%)

Storage period (Months)	Low humidity area	Mavelikkara	Chalakkudy	Kottayam
0	17.5	17.8	17.6	17.5
3	19.4	20.3	20.6	20.5
6	20.0	22.6	23.0	22.9
12	29.0	30.0	30.0	30.0
VR	**	**	**	**
CD ($P \leq 0.05$)	2.7	2.7	2.7	2.76

to be higher for sheets stored in the warehouses.

The increase in Mooney viscosity, initial plasticity and gel content could be attributed to the crosslinking reactions in rubber on storage. Small quantities of certain functional groups are present on the main chain molecule of natural rubber. Crosslinking reactions of these groups with some non-rubber constituents cause the formation of branching in natural rubber, which eventually lead to the occurrence of storage hardening and the formation of gel. Most of the reported work suggests the reaction of aldehyde groups (Sekhar 1960, Subramaniam 1975, Burfield *et al.*, 1987) with certain aldehyde condensing groups in the non-rubber phase including amino acids (Sekhar, 1962; Gregory *et al.*, 1976). Incorporation of additional oxygen containing functional groups such as peroxides, hydroperoxides, alcohols, ketones, aldehydes, epoxides, ethers, esters and carboxylic acids takes place on storage, thereby increasing the

extent of crosslinking (Burfield, 1986).

The infrared spectra of a fresh sheet of rubber and a sheet stored for one year in a warehouse showed that the thermal degradation products of both the samples were similar. The absorption peak of carbonyl group (1710cm^{-1}) had obviously increased during storage indicating higher level of oxidation of the rubber hydrocarbon.

Plasticity retention index

The effect of storage on plasticity retention index (PRI) of the samples is given in Table 6. PRI is a measure of the resistance of raw rubber to thermal oxidative degradation. As the storage period increased, there was significant reduction in PRI of the rubber stored in all the locations. The reduction in PRI was more for the samples stored in the warehouses.

Natural rubber contains small quantity of metals like copper and manganese. These two metals are present in fresh rubber in an inert form, which could be acti-

Table 6. Effect of storage on plasticity retention index

Storage period (Months)	Low humidity area	Mavelikkara	Chalakkudy	Kottayam
0	87	86	85	83
3	86	82	81	80
6	84	79	79	77
12	82	74	75	72
VR	**	**	**	**
CD ($P \leq 0.05$)	2.7	2.77	2.76	2.35

vated to catalyze the degradation process during storage (Yip, 1990). The increase in Po as a result of storage hardening also leads to a reduction in PRI. (Morris, 1991).

Acetone extractables

The effect of storage on the acetone extractables of the samples in the four locations is shown in Table 7. Acetone extractables of natural rubber consist of non rubbers like lipids, sterols, esters and fatty acids. As the storage period increased, there was slight reduction in the acetone extractables. This could be attributed to the condensation and crosslinking of certain lipids thereby making them acetone insoluble.

Strength of raw sheets

The strength of raw sheet rubber, as measured by the breaking load is given in Table 8. As the storage period increased, strength of raw rubber sheets decreased slightly for all the locations. The reduction though not significant, was more for sheets stored in the warehouses.

Visual observation

Sheet samples stored at the three warehouses were affected by mould growth within six months of storage whereas the sheets stored at the low humidity area were unaffected even after one year.

Table 7. Effect of storage on acetone extractables (%)

Storage period (Months)	Low humidity area	Mavelikkara	Chalakkudy	Kottayam
0	3.2	3.3	3.2	3.2
3	3.2	3.1	3.0	3.0
6	3.0	2.8	2.7	2.7
12	2.7	2.5	2.4	2.5
VR	**	**	**	**
CD ($P \leq 0.05$)	0.31	0.34	0.34	0.35

Table 8. Effect of storage on strength of raw sheets (kg/cm)

Storage period (Months)	Low humidity area	Mavelikkara	Chalakkudy	Kottayam
0	31.0	30.8	31.2	30.8
3	30.8	30.5	30.8	30.5
6	30.5	30.2	30.0	30.0
12	30.0	29.7	29.3	29.7
VR	NS	NS	NS	NS

Breakdown characteristics

A typical Haake rheogram is given in Fig 1. As mastication proceeds torque reaches a maximum and then decreases. Torque at the tenth minute can be taken as a measure of the viscosity of masticated rubber. Higher stabilized torque recorded after mastication is indicative of the higher molecular weight of the respective sample. Totalized torque (TTQ) is a measure of the work done during mastication. An important feature of mechanical breakdown is that the rate of degradation is largely governed by the physical state of the rubber. The more viscous the rubber, the greater the work done on it dur-

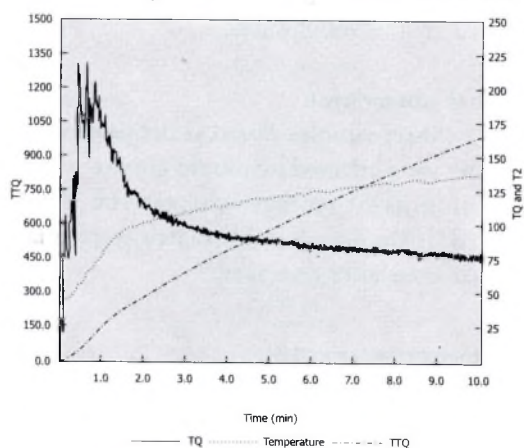


Fig. 1. Haake rheogram of the mix

ing mastication and the more rapid the degradation (Cunneen, 1978).

Table 9 shows the breakdown behaviour of the sheets initially and after storage. For the sheets stored in all the locations as the storage period increased, the TTQ values increased showing that more work has to be done for masticating the samples. The heat generated during mastication is an indication of the state of degradation of rubber. A degraded rubber will probably give less heat during mastication than a virgin rubber (Thomas *et al.*, 1998). As the storage period increased, the heat generated during mastication also increased indicating that no degradation has occurred to the rubber during storage.

Physical properties

The cure characteristics and physical properties of HAF filled vulcanizates prepared from sheet rubber samples are given in Table 10. A slight increase in cure time and scorch time was observed for compounds prepared from sheets stored for one year at all the locations. Hardness, resilience, compression set and heat build up of all the samples were the same initially. DIN abrasion loss was also comparable. The above

Table 9. Effect of storage on breakdown properties

Parameter	Storage period	Low humidity area	Mavelikkara	Chalakkudy	Kottayam
TQ ₅ (Nm)	0	110	120	112	115
	1 year	114	126	118	118
TQ ₁₀ (Nm)	0	100	99	96	99
	1 year	102	110	102	102
$\frac{TQ_5 - TQ_{10}}{5}$	0	2.0	2.8	3.1	3.1
	1 year	2.4	3.0	3.2	3.2
TTQ (Nm-min)	0	1060	1205	1195	1221
	1 year	1115	1253	1313	1248
$\Delta T, ^\circ\text{C}$	0	79	80	85	82
	1 year	80	82	88	83

physical properties of the vulcanizates from stored sheets were almost the same as that of the control samples. This is because the extent of crosslinking/chain scission in the samples during storage was masked by the filler. Tensile and ageing properties of the compounds are given in Table 11. Tensile

strength and modulus at 300% elongation increased slightly after a storage period of one year. Elongation at break was comparable to the original value. Percent retention in tensile strength was slightly higher while the retention in modulus and elongation was slightly lower.

Table 10. Cure and physical properties of HAF filled compounds

Parameter	Storage period	Low humidity area	Mavelikkara	Chalakkudy	Kottayam
Cure time at 150° C (min)	0	10.2	10.5	10.5	10.5
	1 year	11.0	11.0	11.0	11.0
Scorch time at 120°C (min)	0	26	24	26	24
	1 year	25	25	26	25
Hardness (Shore A)	0	45	46	46	46
	1 year	45	48	47	48
Compression set (%)	0	38	38	37	38
	1 year	36	36	37	36
DIN abrasion loss (mm ³)	0	85	88	85	88
	1 year	85	91	90	89
Rebound resilience (%)	0	65	65	65	65
	1 year	65	64	65	65
Heat build-up (ΔT ° C)	0	22	19	21	22
	1 year	22	21	20	21
Tear strength, (N/mm)	0	100	100	100	100
	1 year	99	100	99	98

Table 11. Tensile and ageing properties

Parameter	Storage period	Low humidity area	Mavelikkara	Chalakkudy	Kottayam
Tensile strength (N/mm ²)	0	24.6	28	28.3	28.6
	1 year	22.3	30	30	30
300% modulus (N/mm ²)	0	4.4	6.0	6.0	6.4
	1 year	3.9	6.2	6.5	6.9
Elongation at break (%)	0	876	773	769	736
	1 year	852	770	748	775
Retention in tensile strength (%)	0	78	79	78	78
	1 year	75	82	88	79
Retention in modulus (%)	0	127	133	127	120
	1 year	130	118	123	119
Retention in elongation at break (%)	0	82	89	82	85
	1 year	80	84	82	84

CONCLUSION

Sheets stored at the warehouses were affected by mould growth within six months of storage while no such growth was observed for the sheets stored at low humidity. Mooney viscosity, initial plasticity and gel content of the sheets increased while the plasticity re-

tion index decreased on storage. These changes were less in storage at low humidity and low temperature. Volatile matter increased on storage. Acetone extractables and strength of raw sheets decreased slightly. The technological and ageing properties were not significantly affected by storage.

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