Indian Journal of Natural Rubber Research, 8(1) : 1-7, 1995

INFLUENCE OF STORAGE ON PROPERTIES OF NATURAL RUBBER LATEX CONCENTRATE AND VULCANIZATES

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Claramma, N.M., Varghese, L. and Mathew, N.M. (1995). Influence of storage on properties of natural rubber latex concentrate and vulcanizates. *Indian Journal of Natural Rubber Research* , 8(1) : 1-7.

High ammonia and low ammonia preserved centrifuged latices were stored for a period of 18 months. Effect of storage on properties of the latices and vulcanizates prepared therefrom was investigated. Mechanical stability time, zinc oxide viscosity, potassium hydroxide number and volatile fatty acid number were found to be affected by storage. Physical properties of vulcanizates were more or less unaffected by storage of latices up to six months, but beyond this period, decrease in properties was observed. Ageing resistance of the vulcanizates was also found to be affected by the storage period of latices.

Key words: Natural rubber latex, Mechanical stability time, Zinc oxide viscosity, Potassium hydroxide number, Volatile fatty acid number, Latex vulcanizate, Ageing.

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INTRODUCTION

In India about 12 per cent of the natural rubber produced is processed into latex concentrate. During pumping, transportation and storage, latex is subjected to mechanical agitation, aeration and even temperature variation. It is known that the chemical composition of latex changes significantly due to the action of bacteria, enzymes and preservatives. These changes in chemical composition are reflected in the properties of latex particularly, mechanical stability time (MST), volatile fatty acid (VFA) number and potassium hydroxide (KOH) number and hence they received the most attention. Several investigations have been carried out on the changes in properties of latex concentrate on storage. Collier (1955) observed a progressive decrease in mechanical stability of centrifuged latex stored under anaerobic conditions, which prevailed in an almost fully filled container. He noted an increase in mechanical stability of latex when there was an appreciable air space in the container. He also reported that increase of VFA of latex concentrate was more pronounced when it was stored in anaerobic conditions. Lowe (1960) reported that pumping of latex concentrate accelerated the formation of VFA. Pillai (1968), however, reported that commercial pumping operation did not have any deleterious effect on the properties of latex. Reports of RRIM (1971) indicated that MST, VFA and KOH number of latex concentrate increased on storage and MST is particularly affected by storage temperature . According to Chin *et al.* (1979), although storage of latex affects its primary properties, the physical properties of vulcanized rubber films prepared from the stored latex are not adversely affected for a storage period of up to eight months .

This paper reports a comparative evaluation of high ammonia and low ammonia preserved natural rubber latex concentrates with respect to the effect of storage on primary properties of latex and physical properties and ageing characteristics of vulcanizates prepared therefrom.

MATERIALS AND METHODS

High ammonia and low ammonia preserved centrifuged latices were freshly prepared and stored for a period of upto 18 months. The properties of latices and their vulcanizates were tested periodically.

Fresh field latex (400 litres) was collected from the Central Experiment Station of the Rubber Research Institute of India and ammoniated to 0.3 per cent. From this 200 litres were transferred to one barrel and ammoniated to 1 per cent. To the rest of the latex, 0.025 per cent each of zinc oxide and tetramethyl thiuram disulphide were added as dispersions and kept in another barrel. After desludging, the two latex batches were centrifuged separately using an α-Laval centrifuge (Model LRB 510). The centrifuged latex from the first barrel was ammoniated to 0.7 per cent (HA latex) and that from the second barrel was ammoniated to 0.25 per cent . To the second (LATZ), 0.05 per cent ammonium laurate was also added.

The latex samples were periodically tested for total solids content (TSC), dry rubber content (DRC), mechanical stability time (MST), potassium hydroxide (KOH) number, volatile fatty acid (VFA) number, viscosity, zinc oxide viscosity (ZOV) and alkalinity. For determining strength properties, the latices were compounded as per the formulation given in Table 1. After maturation, thin films were cast from the latices in shallow glass dishes to a thickness of approximately 1 mm. After drying, the films were vulcanized in an air oven at 100° C for one hour. Samples were aged at 70° C for 7, 14 and 21 days. The vulcanizates were tested for tensile properties before and after ageing as per ASTM D 412 (1994) using a Zwick Universal Testing Machine model 1474.

RESULTS AND DISCUSSION

Table 2 shows the effect of storage of HA and LATZ latices on TSC, DRC, and ammonia content. It can be seen that TSC

Table 1. **Formulation**

Ingredients	Parts by weight (wet)
Centrifuged latex, 60%	167.0
Potassium hydroxide solution, 10%	2.5
Sulphur dispersion, 50%	2.0
Zinc diethyldithiocarbamate dispersion, 50%	1.0
Zinc oxide dispersion, 50 %	0.4

Table 2. Effect of storage of latex on TSC, DRC and ammonia content

Period of storage (months)	TSC (%) HA	TSC (%) LATZ	DRC (%) HA	DRC (%) LATZ	Ammonia content (%) HA	Ammonia content (%) LATZ
0	61.45	61.70	60.15	60.25	0.81	0.29
1	61.50	61.65	60.10	60.11	0.81	0.29
2	61.56	61.62	60.18	60.21	0.81	0.28
4	61.43	61.61	60.10	60.22	0.74	0.24
6	61.40	61.65	59.90	60.08	0.73	0.24
12	61.34	61.60	60.10	60.00	0.72	0.21
18	61.33	61.70	59.84	60.00	0.71	0.20

and DRC of the two latices are more or less unaffected by storage up to 18 months. A slight decrease in ammonia content is observed during the above period. Table 3 shows the effect of storage of latex on viscosity. For HA and LATZ latices, a slightly higher viscosity is observed initially which decreases on storage for one month and thereafter is maintained more or less constant.

Table 3. **Effect of storage of latex on viscosity**

Period of storage (months)	Brookfield viscosity (Ns/m²)			
	HA		LATZ	
	5 rpm	50 rpm	5 rpm	50 rpm
0	0.14	0.077	0.12	0.070
1	0.13	0.074	0.11	0.067
2	0.13	0.074	0.11	0.067
4	0.13	0.075	0.11	0.067
6	0.13	0.073	0.11	0.068
12	0.13	0.074	0.11	0.067
18	0.13	0.073	0.11	0.066

Table 4 shows the effect of storage of latex on zinc oxide viscosity. For HA and LATZ latices zinc oxide viscosity increases on storage. For LATZ latex the increase is very slow compared to that of HA latex. HA latex shows a very rapid rise in zinc oxide viscosity during storage and after a storage period of one year the latex gets coagulated during the test. The lower stability of HA latex to zinc oxide is due to the higher ammonia content and the ammonium ions of the latex, which cause more zinc oxide to dissolve in the serum (Cockbain and Philpott, 1963).

Table 4. **Effect of storage of latex on zinc oxide viscosity**

Period of storage (months)	Zinc oxide viscosity (Ns/m²)	
	HA	LATZ
0	0.072	0.044
1	0.080	0.048
2	0.084	0.050
3	0.104	0.052
4	0. 120	0. 052
5	0.392	0.060
6	O . 720	0. 068
7	out of range	0. 084
12	coagulated	0.104

Table 5 shows the effect of storage of latex on VFA and KOH numbers. VFA consists mostly of formic, acetic and propionic acids, resulting from the bacterial attack on substrates present in latex (Blackley, 1966 a). The magnitude of VFA number , is therefore a good index of the state of preservation of latex. For both types of latices, VFA number slightly increases on storage. LATZ latex has lower VFA number than HA latex during storage up to one year. The difference is more pronounced during the early period of storage. In other words when the storage period of latex was above three months the difference in VFA of

Table 5. **Effect of storage of latex on VFA and KOH numbers**

Period of storage (days)	VFA number		KOH number	
	HA	LATZ	HA	LATZ
6	0.017	0.006	0.40	0.48
15	0.023	0.008	0.41	0.49
20	0.023	0.009	0.54	0.59
30	0.024	0.011	0.54	0.60
60	0.026	0.019	0.54	0.60
90	0.027	0.025	0.56	0.64
120	0.027	0.025	0.56	0.64
150	0.028	0.025	0.56	0.66
180	0.028	0.024	0.60	0.72
365	0.033	0.030	0.62	0.77
545	0.048	0.096	0.78	1.10

HA and LATZ latex narrows down and on keeping the latex for 18 months, LATZ latex exhibited a higher VFA number than HA latex, though still within permissible limits.

The KOH number of HA and LATZ latices increased during storage (Table 5) which indicates a growth in concentration of acids which are present as ammonium salts (Blackley, 1966 b).

Table 6 shows the effect of storage of latex on MST. Results show that, for fresh latex MST was very low and it rises during storage. For HA latex during the first 20 days, the rate of increase in MST was very rapid, followed by a slower increase. The maximum MST was observed in 75 days of storage and afterwards a slow decrease has been noted. The higher MST values for LATZ latex is due to the presence of added ammonium laurate during its preparation. In fresh latex the protective layer of rubber particles consists mainly of proteins and phospholipids. When ammonia is added to latex, hydrolysis of proteins occurs slowly, but that of the phospholipids occurs more rapidly to fatty acid anions and other products. The liberated fatty acid anions are adsorbed at the particle interfaces and thus enhance the stability of latex due to a higher surface charge and therefore a higher repulsive energy between particles . This accounts for the increase in MST of ammonia preserved latex during the first few months of storage. As the latex ages further, the composition of protective layer again changes (Cockbain and Philpott, 1963) . This change along with the increase in ionic strength of the aqueous phase of latex, causes the observed reduction in MST when the latex is stored for one year and above.

Table 6. **Effect of storage of latex on MST**

Period of storage (days)	MST (seconds)	
	HA	LATZ
6	125	>1200
10	293	>1200
15	607	>1200
20	816	>1200
25	885	>1200
50	980	>1200
60	1160	>1200
75	1395	>1200
90	1300	>1200
120	1211	>1200
160	1029	>1200
180	1028	>1200
365	872	>1200
545	387	1200

Physical properties of vulcanized films

Figure 1 shows the effect of storage of HA and LATZ latices on the tensile strength of vulcanizates. The tensile strength is unaffected by storage of latex up to three months. But thereafter it decreases slowly upto six months and then rather rapidly. Modulus at 100 per cent elongation and elongation at break (Figures 2 and 3 respec-

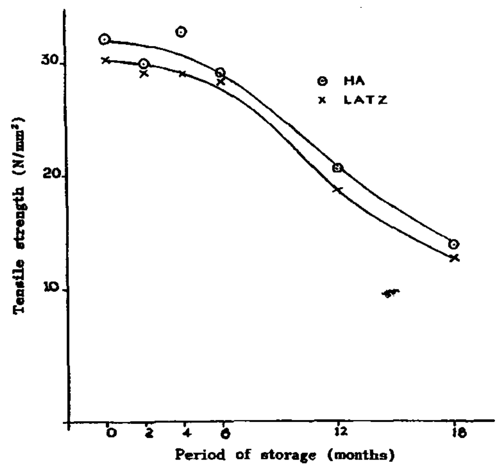

Fig. 1. Effect of storage of latex on tensile strength

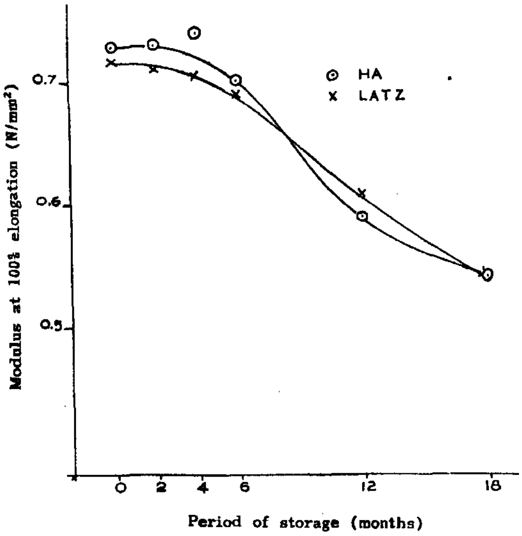

Fig. 2. Effect of storage of latex on modulus at 100% elongation

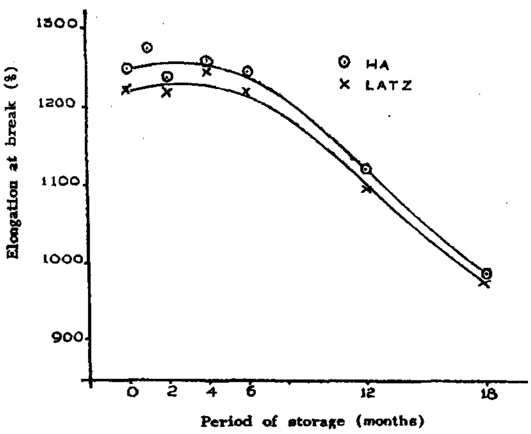

Fig. 3. Effect of storage of latex on elongation at break

tively) also show the same trend. Table 7 shows the effect of storage of HA and LATZ latices on volume fraction of rubber (Vr) in the swollen vulcanizates. A decrease in Vr is noted when the latex is stored for long periods. Vr can be taken as a measure of crosslink density. Tensile strength is strongly dependent upon crosslink density of the vulcanizate (Glazer and Cotton, 1961). A

Table 7. **Effect of storage of latex on volume fraction of rubber**

Period of storage (months)	Volume fraction of rubber (Vr)	
	HA	LATZ
0	0.1676	0.1670
12	0.1562	0.1559
18	0.1442	0.1444

decrease in Vr is indicative of the decrease in tensile strength of the vulcanizate when the latex is stored for long periods .

Ageing behaviour

Table 8 shows the effect of ageing of vulcanizates obtained from HA and LATZ

Table 8. **Effect of storage of latex on tensile strength after ageing**

Period of Storage (months)		Tensile strength (N/mm²) after ageing for different periods (days)			
		0	7	14	21
0	HA	31.9	28.0	27.3	21.7
	LATZ	30.7	27.1	24.7	18.0
6	HA	29.2	21.5	13.9	5.3
	LATZ	28.7	20.1	11.4	4.2
12	HA	20.3	14.9	5.5	–
	LATZ	18.5	15.6	5.0	–
18	HA	14.0	5.0	–	–
	LATZ	13.0	4.8	–	–

latices which had been stored for different periods, on tensile strength. It can be seen that tensile strength of vulcanizates decreases on ageing. But the rate of decrease was less for fresh latex. As the period of storage increases the rate of decrease in tensile strength was more pronounced. Table 9 shows the effect of ageing of vulcanizates on modulus at 100 per cent elongation. It can be seen that modulus decreased as the ageing period of vulcanizate was increased. The rate of decrease was more when the storage period of latex was longer.

Table 9. **Effect of storage of latex on modulus at 100% elongation after ageing**

Period of storage (months)		Modulus at 100% elongation (N/mm^2) after ageing for different periods (days)			
		0	7	14	21
0	HA	0.73	0.70	0.68	0.67
	LAT Z	0.72	0.70	0.66	0 .63
6	HA	0.70	0.68	0.65	0.53
	LATZ	0.69	0.67	0.63	0.49
12	HA	0.59	0.57	0.45	-
	LATZ	0.61	0.54	0.42	-
18	HA	0.54	0.48	-	-
	LATZ	0.54	0.43	-	-

Table 10 shows the effect of ageing of vulcanizates on elongation at break. In this case also as the storage period of latex increased, elongation at break after ageing decreased and the rate of decrease was higher for vulcanizates obtained from latex which had been stored for long periods.

Table 10. **Effect of storage of latex on elongation at break after ageing**

Period of storage (months)		Elongation at break (%) after ageing for different periods (days)			
		0	7	14	21
0	HA	1252	1238	1220	1192
	LATZ	1225	1256	1234	1210
6	HA	1246	1158	1072	875
	LATZ	1213	1180	1065	844
12	HA	1117	1005	920	-
	LATZ	1096	956	901	-
18	HA	989	890	-	-
	LATZ	974	908	-	-

The presence of materials which exert an antioxidant effect in latex has been recognized for many years (Noble, 1953). Choline compounds present in latex are vulcanization accelerators and show antioxidant properties in raw rubber (Archer *et al.*, 1963). During storage, latex undergoes changes associated with bacterial and hydrolytic actions. Changes will also be effected by many factors including handling, seasonal effect, pumping and whether latex is in bulk or in drums. Hence it can be concluded that during long term storage the natural antioxidants present in latex get converted to other products and/or are used up, which causes a reduction in ageing resistance of the vulcanizates.

CONCLUSION

DRC and TSC of high ammonia and low ammonia latices are unaffected by storage of latex up to 18 months. Freshly prepared latex exhibited a slightly higher initial viscosity which decreased during one month storage and remained rather constant on further storage. Zinc oxide viscosity increased during storage of latex. For LATZ latex the increase was very slow. However, HA latex showed a very rapid rise in ZOV as the latex ages. VFA number of HA and LATZ latices slightly increased on storage and LATZ latex exhibited a lower initial VFA number than HA latex. But on storage the difference narrows down and after a period of 18 months, LATZ latex exhibited a higher VFA than that of HA latex, but within permissible limits. KOH number of the latices also increased on storage.

Physical properties of latex vulcanizates were more or less unaffected by storage of latex up to six months. But beyond this period, decrease in tensile properties was observed. Ageing resistance of the vulcanizates was also found to be affected by the storage period of latex. When the storage period was beyond one year, the rate of decrease in ageing resistance was more for both latices.

ACKNOWLEDGEMENT

The authors are grateful to Dr.M.R.Sethuraj, Director, Rubber Research Institute of India for providing facilities for the study. The co-operation extended by the Department of Processing and Product Development is also gratefully acknowledged.

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