STUDIES ON ACCELERATED AGEING TESTS FOR QUALITY PARAMETERS OF CONCENTRATED NR LATEX

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ABSTRACT

A method for prediction of important quality parameters of concentrated latex like mechanical stability time (MST), viscosity and KOH number are presented. Ageing of latex at 50^0 C for 96 hours keeping ammonia level at 1% (w/v) accelerated the chemical changes that normally take place during storage and results in a change in its quality parameters. Ageing at other temperatures of 45,60 0r 70 ^{0} C for about the same duration did not correlate with the chemical changes that took place during storage. Hydrolysis of phospholipids leading to the formation of fatty acid soaps that increased the MST of latex was the prominent reaction along with hydrolytic reactions of proteins during ageing at 50 ^{0} C. Formation of organic acids that adversely affected MST was predominant as compared to formation of long chain fatty acids at 60 and 70^0 C while these reactions were slow at 45^0 C. The important long chain fatty acids formed in latex during ageing at 50^{0}C for 96 h analysed by a liquid chromatographic technique were lauric, myristic, linolenic, linoleic, palmitic, oleic and stearic acids. The quantity of these long chain fatty acids formed during accelerated ageing were found to be comparable to those formed during storage at room temperature for one month. Statistical analysis reveled that the absolute difference between predicted and actual MST values during storage was significantly lower than 100,150 and 200 seconds for the first, second and third month respectively. The absolute mean of the difference between predicted and actual viscosity values was significantly less than 7.71 during storage up to three months. The volatile fatty acid (VFA) number could not be predicted, as the bacterial action taking place at room temperature could not be accelerated at high temperatures. The KOH number

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predicted during storage was lower than the actual KOH number .The accelerated test was useful in predicting quality parameters of different types of lattices that showed a wide variation in storage behaviour.

INTRODUCTION

The important quality parameters of latex like mechanical stability time (MST), viscosity KOH number, etc. included in the international specifications[1-2] change during storage of latex[3]. These changes that take place at a fast rate during the early period of storage, are attributed to mainly chemical effects of ammoniation[4-5] and formation of volatile fatty acids[6]. The phospholipids[7] and proteins[8] mainly α-globulin[9] adsorbed to the rubber particles play a vital role in maintaining its colloidal stability. Phospholipids undergo alkaline hydrolysis to form long chain fatty acids [10-11] that react with ammonia to form soaps and adsorption of these negative anions on rubber particles increases its MST during storage[12]. The proteins also undergo change to low molecular weight peptides[13] and aminoacids[14] that decrease its MST during storage. The volatile fatty acids formed during storage by bacterial action also decrease MST of latex. The increase in MST by temperature irrespective of conditions like aerobic or anaerobic has been reported earlier[15] and Sinclair et al[16] established aging conditions that increase the MST and KOH number of concentrated latex for prediction of future quality of latex. A standard curve based on the MST generated during storage for several lots of latex had been used earlier to predict behaviour of latex during storage in Malaysia.

Usually several months elapse between the production of latex and its conversion into useful product. The requirement of quality parameters varies widely among the latex based products. What the customer requires is the actual values of these quality parameters when the latex arrives at his site. It will be highly useful if we can predict the quality parameters of latex that will be attained during storage, immediately after its production with a reasonable accuracy. So far there has been no systematic reports on prediction of quality parameters of latex and this work is an attempt in this line. In this work the change in values of quality parameters such as MST, KOH number and viscosity obtained by accelerated ageing was correlated with quantity of higher fatty acids formed during accelerated ageing. A comparison of these values with those formed by natural storage of latex was also made.

EXPERIMENTAL

Centrifugally concentrated latex was obtained from various factories located in different districts of Kerala. An initial trial conducted by using different temperatures (45,50,60 and 70^{0}C), time of heating (24,48,72 and 96 h) and level of ammoniation (0.75 and 1%) indicated that accelerated ageing of latex done at 50° C for 96 h keeping the ammonia level at 1%, gave results which correlated well with results obtained after natural storage of latex. Hence further work was done keeping these conditions for the accelerated ageing of latex. Accelerated ageing of latex was done by heating about 500 ml of the homogenized latex taken in an amber coloured bottle after addition of ammonia so as to be of 1% (w/v), in an air oven, at 50° C for 96 h. The bottle containing latex was kept slightly loosely stoppered to ensure that ammonia is not lost during heating. The initial results obtained were confirmed by a detailed experiment involving sixteen samples collected from different sources and analyzing the data statistically.

The quality parameters of latex were determined by test procedures as per the relevant international standards. The extraction of fatty acids was carried out as reported earlier[11] using isopropanol and separation of fatty acids was carried out by liquid chromatography.

Procedure for extraction of fatty acids

15 g of concentrated latex diluted with 15 g of distilled water was added drop wise to 140 ml isopropyl alcohol. After complete addition, stirring was continued for 2 hours after which the isopropyl alcohol was decanted. The rubber was washed with 80 ml of isopropanol, decanted and immersed overnight in 80 ml of fresh alcohol. The isopropyl extracts were combined and isopropanol removed by distillation. The dry extract was dissolved in 15 ml 0.1 N KOH solution, aqueous solution was completely transferred to 50 ml beaker and then acidified with dil HCl to a pH of 2. The fatty acids formed were extracted with diethyl ether three times, using 50 ml each time. The ether extracts were collected and evaporated to dryness on a water bath.

Procedure for separation and quantification of fatty acids

This residue that contained the fatty acids was dissolved in 40 ml of solvent mixture $THF/CH_3CN/H_2O$ in the ratio 25:45:35 by volume. The separation of fatty acids was done by using Waters fatty acid column as per details given:

Instrument	- Waters LC system
Detector	- Waters 410 Differential refractometer
Pump	- Waters 510 pump
Flow rate	- 1 ml/minute
Temperature	- 40^0 C.

RESULTS AND DISCUSSIONS

1 Accelerated ageing

The effect of ageing as measured by MST for latex containing 1 % ammonia at four different temperatures is shown in Table 1. On ageing at 45^0C the MST increase is slow with duration whereas at 50^0C the MST build-up is faster and levels off after ninety six hours. During high temperature ageing the MST build-up is low and increases up to forty eight hours for 60° C, while at 70° C there is an initial increase in MST for 24 hours followed by a drastic fall with further ageing. An increase in MST during heating for shorter duration at 60 and 70° C followed by a decrease at higher temperatures has been reported earlier[17].The amount and type of fatty acids produced during accelerated ageing, separated by liquid chromatography is shown in Fig 1. The important fatty acids formed during hydrolysis of phospholipids correspond to lauric, myristic, linolenic , linoleic , palmitic, oleic and stearic acids as reported earlier by gas chromatographic techniques[18,11]. As seen from the chromatograms fatty acids are formed during ageing at 50 and 60° C while that formed at high temperature of 70° C is considerably low.

A measure of total acids which include the higher fatty acids, the volatile fatty acids and other organic acids as obtained from the KOH number is shown in Table 2. As observed the KOH number increases with duration and temperature of ageing which shows that acidic materials are formed during high temperature ageing from hydrolysis of proteins. The volatile fatty acid number given in Table 3 reveals that quantity of volatile fatty acids formed are very low during accelerated ageing. Two types of reactions[17] that occur during storage of latex and expected to take place during accelerated ageing are

1. Hydrolysis of phospholipids that produce higher fatty acids which increase the colloidal stability
2. Hydrolysis of proteins resulting in amino acids which have a destabilizing effect on latex.[19]

At high temperature of 70° C it may be possible that either fatty acids formed undergo changes[4] to low molecular weight fractions that do not stabilize latex or level of hydrolysis reaction is very low and proteins are either denatured[20-21] or undergo hydrolysis to low molecular weight organic acids resulting in a comparatively low MST. At 60° C hydrolysis reactions of both phospholipids and proteins occur at a faster rate and hydrolytic products of proteins contribute adversely to MST build up. Consequently viscosity of latex increases during high temperature ageing. (Table 4). During ageing at temperatures of 45 and 50° C hydrolysis of phospholipids with the formation of fatty acids is a dominating reaction along with other chemical changes that result in an increase in MST and decrease in viscosity. These results suggest that during ageing at 50° C for ninety-six hours a chemical change is accelerated that would have otherwise occurred naturally during storage. The amount of fatty acids formed during storage of latex as compared with accelerated ageing is given in Table 5. The total fatty acids produced during accelerated ageing and storage is very close, showing that the hydrolytic reaction of phospholipids is replicated during ageing and is comparable to that obtained during storage[17]. The levels of quality parameters obtained during accelerated ageing thus become very close to that obtained during storage for 1 month (Table 6).

2 The storage behaviour of latex and application of accelerated ageing test for prediction of quality parameters.

Commercially obtained centrifuged latex showed a wide variation in initial MST. It is well known that initial MST of freshly prepared concentrated NR latex is low and an increase in MST is obtained either by storage or by externally added soaps. The high initial MST shown by some of the lattices can be due to the long chain fatty acid soaps formed in preserved field latex, a part of which goes to the concentrate during centrifugation or presence of externally added soap. As can be observed from Table 7, MST increased slowly during storage up to six months or attained a maximum in a period of three months followed by a decrease or it may decrease during storage. The MST increases at a fast rate during the early period of storage because the hydrolysis of phospholipids leading to an increase in MST is almost complete during the first twenty days of its production while the hydrolysis of proteins occur during the later period of storage[17]. An increase in MST of latex on storage for longer period which was attributed to the aerobic conditions prevailing during storage was noted earlier by Collier[22] and Chen et al[12]. As the VFA does not increase appreciably of a well preserved latex during storage, the observed increase in MST up to six months could be due to adsorption of fatty acid soaps in the aqueous serum[11] at vacant sites formed by hydrolysis of proteins as some proteins associated with rubber particles are removed only slowly by alkaline hydrolysis[23]. For centrifuged latex prepared from aged field latex, phospholipids would be exhausted by hydrolysis and the amount of fatty acids produced during storage of the concentrate will be negligible resulting in a decrease in MST. The MST predicted by accelerated ageing is very close to MST obtained during storage in all these cases. Consequently the viscosity predicted is also very close to the values obtained during storage. The increase in volatile fatty acids is a slow process that normally takes place during storage due to microbial action at ambient temperature. The VFA number cannot be predicted by accelerated ageing test done at high temperature (Table 8). Consequently the KOH number predicted is also lower than the actual KOH number (Table 9) as the acids obtained by the hydrolytic reactions of proteins and phospholipids are only accounted here. On statistical analysis it is found that (Table.11) the absolute difference between the predicted and actual MST is significantly lower than 100,150 and 200 for the first, second and third months respectively and the average absolute mean is 61,71 and 108 respectively for the above periods. The absolute mean of predicted viscosity is less than 7.71 cps for storage of three months. The predicted KOH number is always lower than the actual value for all the three months of storage.

3 Effect of externally added soap and application of accelerated ageing test for prediction of quality parameters.

It is a customary practice among latex processors to boost the MST of freshly prepared concentrated latex by the addition of a small quantity of higher fatty acid soap such as ammonium /potassium laurate. Hence the effect of addition of soap into latex on the prediction of quality parameters was also examined in this study. The effect of externally added soap on MST is shown in Table 12. The initial MST increased greatly by addition of soap. The MST increased by ten folds by addition of 0.03 % potassium laurate soap. The predicted MST and viscosity values are however close to the values obtained during storage in all these cases while the KOH number is lower than the KOH number obtained during storage.

CONCLUSION

Accelerated ageing of latex treated with ammonia to a level of 1 % at 50 ^{0} C for 96 hours without loss of ammonia predicts with reasonable accuracy the quality parameters obtained during its storage. The MST can be predicted with an accuracy of 100 seconds for the first month 150 seconds for the second month and 200 seconds for the third month, The absolute mean of the difference between predicted and actual viscosity values was significantly less than 7.71 cps during storage for three months. The KOH number predicted is lower than the actual KOH number realized during storage and the VFA number cannot be predicted accurately. The observations on MST were found to correlate with the amount of higher fatty acids formed during accelerated ageing of latex at 50° C for 96 h and storage at ambient temperature for two to three months.

Table 1 MST of latex aged at different temperatures, sec.

Temperature of ageing, °C	Duration of ageing, hours				
	24	48	72	96	120
45	210	319	695	765	800
50	600	747	786	900	900
60	349	410	400	390	-
70	341	180	120	-	-

Table 2. KOH number of latex aged at different temperatures.

Temperature of ageing, °C	Duration of ageing, hours			
	24	48	72	96
50	0.5510	0.5560	0.5762	0.5901
60	0.5635	0.5680	0.5745	0.6010
70	0.5710	0.6010	0.6269	0.6346

Table 3. VFA number of latex aged at different temperatures.

Temperature of ageing, °C	Duration of ageing, hours			
	24	48	72	96
50	0.0118	0.0100	0.0120	0.0127
60	0.0118	0.0120	0.0123	0.0140
70	0.0104	0.0145	0.0170	0.0194

Table 4 Viscosity of latex aged at different temperatures, cps.

Temperature of ageing, °C	Duration of ageing, hours			
	24	48	72	96
50	140	128	124	122
60	156	154	150	146
70	176	176	170	170

Table 5. Quantity of fatty acids formed during storage, g/100g latex

Storage period	Lauric	Myristic-	Llinolenic	Linoleic	Palmitic	Oleic	Stearic	Total higher fatty acids
One day	0.0250	trace	0.0290	0.1465	0.0404	0.0560	0.0670	0.3639
20 days	0.0426	0.0240	0.0320	0.1865	0.0505	0.1100	0.0846	0.5302
40 days	0.0546	0.0500	0.0350	0.2100	0.0613	0.1200	0.1440	0.6749
Accelerated ageing	0.0453	0.0509	0.0340	0.2100	0.0600	0.1200	0.1443	0.6632

Table 6. MST, KOH number and VFA of latex after storage and accelerated ageing

Storage period	MST, seconds	KOH number	VFA number	Viscosity, cps
One day	120	0.5600	0.0104	156
30 days	938	0.6311	0.0184	144
Accelerated ageing	900	0.5901	0.0127	142

Table 7. Predicted and actual MST of typical commercial latex samples, seconds

Sl. No.	One day	Predicted	MST in seconds during storage, period			
			1 month	2 months	3 months	6 months
1	450	570	540	540	547	554
2	450	824	730	756	978	1020
3	570	885	785	876	1046	600
4	90	500	400	605	700	584
5	120	630	650	748	772	600
6	110	460	370	506	650	605
7	510	640	540	518	419	420
8	750	675	675	670	670	424

Table 8. Predicted and actual VFA number of typical commercial latex samples

Sl. No.	One day	Predicted	VFA number during storage, period			
			1 month	2 months	3 months	6 months
1	0.0880	0.0955	0.1011	0.1089	0.1036	0.1073
2	0.0342	0.0363	0.0407	0.0449	0.0520	0.0595
3	0.0110	0.0125	0.0198	0.0294	0.0350	0.0397
4	0.0117	0.0122	0.0218	0.0279	0.0292	0.0337
5	0.0253	0.0263	0.0317	0.0335	0.0393	0.0453
6	0.0245	0.0250	0.032	0.0345	0.0454	0.0485
7	0.0255	0.0265	0.0267	0.0345	0.0374	0.0405
8	0.0180	0.0237	0.055	0.0696	0.0708	0.0760

Table 9. Predicted and actual KOH number of typical commercial latex samples

Sl. No	One day	Predicted	KOH number during storage, period		
			1month	2 months	3 months
1	0.7133	0.7768	0.8588	0.9260	0.9767
2	0.6237	0.6718	0.7049	0.7520	0.7865
3	0.4212	0.4511	0.4810	0.5131	0.5395
4	0.3948	0.4560	0.4697	0.5015	0.5475
5	0.3980	0.5118	0.5216	0.6257	0.6277
6	0.4797	0.5414	0.6142	0.7118	0.7400
7	0.5722	0.5872	0.6230	0.6865	0.6924
8	0.6234	0.7370	0.7593	0.8302	0.8364

Table 10. Predicted and actual viscosity of typical commercial latex samples, cps

Sl. No.	One day	Predicted	Viscosity during storage, period		
			1month	2 months	3 months
1	224	210	200	208	208
2	156	124	134	130	116
3	220	180	178	173	164
4	144	120	122	104	106
5	88	84	86	86	84
6	108	92	108	106	102
7	144	128	130	128	126
8	192	140	132	128	126

Table 11. Statistical data of predicted and actual values of quality parameters of centrifuged latex concentrate from sixteen sources.

Period of storage, months	MST, seconds			Viscosity, cps			KOH number		
	Mean	SD	t	Mean	SD	t	Mean	SD	t
ONE	65.12	37.08	-3,88**	7.71	5.43	-6.29**	-0.031	0.026	-4.916**
TWO	71.29	48.31	-6.72**	7.24	4.70	-7.68**	-0.077	0.048	-6.614**
THREE	108.41	64.43	-5.86**	6.88	4.95	-7.60**	-0.095	0.057	-6.87**

** Significant at probability < 0.01

Table 12. The effect of externally added soap on quality parameters of concentrated NR latex

Quality parameter	Quantity of soap, phr	One day	Predicted	One month
MST, seconds	0.000	187	1210	1200
	0.005	202	1350	1310
	0.010	248	1495	1440
	0.015	295	1710	1800
	0.020	379	2050	2040
	0.025	428	2350	2340
	0.030	563	2500	2600
Viscosity, cps	0.000	134	112	110
	0.005	132	110	108
	0.010	130	108	106
	0.015	128	106	104
	0.020	122	100	98
	0.025	116	98	96
	0.030	114	96	94
KOH number	0.000	0.3635	0.4713	0.5005
	0.005	0.4001	0.4800	0.5005
	0.010	0.4180	0.4846	0.5100
	0.015	0.4212	0.4992	0.5213
	0.020	0.4489	0.5149	0.5300
	0.025	0.4672	0.5813	0.5612
	0.030	0.4711	0.5452	0.5717

REFERENCES

1. ISO 2004- 1979 (E) Rubber latex, natural-centrifuged or creamed, ammonia-preserved types – specification Vol 1.
2. 2. ISO 2027 – 1978 (E) Rubber, natural latex, evaporated preserved-specification Vol. 1.
3. 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 nat. Rubb. Res.* 8, 1
4. ALTMAN, R.F.A. (1946) Chemical changes in ammoniated Hevea latex *Transactions of IRI*, 22, 302
5. COCKBAIN, E.G. and PHILIPOT, M.W. (1963) The chemistry and physics of Rubber like substances L Bateman. Ed. Mclaren London chapter 4.
6. BLACKLEY, D. C. (1997) *Polymer Latices Science and Technology*, Vol 2. Types of lattices, Chapman and Hall Publishers, 105-114
7. HASMA, H. (1991) Lipids associated with rubber particles and their possible role in mechanical stability of latex of latex concentrate. *J. nat. Rubb. Res.* 6, 105
8. ARCHER. B.L. (1960) Proteins of *Hevea brasiliensis* latex *Biochm. J.*75, 236
9. ABI SANTHOSH APREM and SATYENDRA NATH PAL (2000) Latex allergy and recent developments in deproteinisation of natural rubber latex. *J nat. Rubb. Res.* 5, 94
10. PENDLE, T.D. and GORTON A.D.T. (1978) The mechanical stability of natural rubber latexes. *Rubber Chem. Technol.* 51, 986
11. SEONG-FONG CHEN and CHIEW-SUM NG (1984). The natural higher fatty acid soaps in natural rubber latex and their effect on the mechanical stability of the latex. Rubber *Chem. Technol.* 57, 243
12. CHEN SEONG-FONG and NG CHIEW-SUM, (1984). The effect of natural higher fatty acid soaps in natural rubber latex on the mechanical stability of the latex. *NR Technology* 15, 54.
13. HASMA, H. and AMIR-HASHIM, M.Y. (1997) Changes to NR latex proteins on processing the latex to products, *J nat. Rubb Res*, 12, 21
14. KASINATHAN, M NADARAJAH. and TIRIMANNE, A.S.L.(1971) A study of free amino acids in the latex of natural rubber, *RRIC Bulletin* 6, 29

15. Rubber Research Institute of Malaya, *Planter's Bulletin* (1971) Latex concentrate properties and the effect of storage and handling, 113,102

16. SINCLAIR, E.A and JANSSEN, F.W. (1972). Accelerated maturing of fresh natural latex concentrate, *Polymer J.* 4, 93

17. DAVIES, R.T. and PENDLE, T.D.(1991).Thermally induced changes in the mechanical stabilities of natural rubber latex concentrates,*J.nat. Rub. Res.*6, 12

18. CRAFTS, R.C. DAVEY, J.E. McSWEENEY G.P. and STEPHENS, I. S. Comparison of free fatty acid values with individually determined organic and inorganic acid concentrations in the extracts of Malaysian natural rubber, *J nat. Rubb. Res.* 5, 275

19. CHIN, H.C. and SINGH, M..M. and LOCKE, S.E. (1979) Effect of storage on the properties of high-ammonia preserved Hevea latex concentrate, *Plastics and Rubber; Matreials and Applications* 11,164

20. RUSDAN DALIMUNTHE, Effect of dicumyl peroxide on mechanical stability time of concentrate latex, *International Rubber Conference*, Kuala Lumpur 1997 p 65

21. RUSDAN DALIMUNTHE (1993) Effect of styrene on mechanical stability time of natural rubber latex before modification. *Report of the Proceedings of the International Rubber Technology Conference*, Kuala Lumpur, Malaysia, ED. Abdul Aziz bin Kadir p 455

22. COLLIER, H.M. (1955) Effect of storage condition on the properties of latex-Part 1 *Transactions of IRI*, 31, 166.

23. HASMA, H. (1992) Proteins of natural rubber latex concentrate, *J. nat Rubb. Res*, 7, 102.

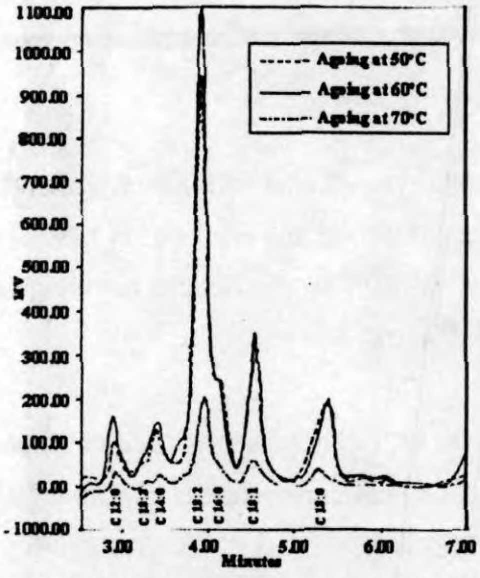

Fig 1. Chromatograms showing separation of fatty acids from natural rubber latex aged at 50°C, 60°C and 70°C.