

Thermally-induced Changes in the Mechanical Stabilities of Natural Rubber Latex Concentrates

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This paper describes an investigation of the increased mechanical stability obtained by heating latex concentrate at 60°C for limited periods. The present study suggests that this does not result from chemical changes due, for example, to accelerated hydrolysis. The heating process appears to affect only the mechanical stability of the latex and the associated property of zinc oxide mechanical stability. It is tentatively suggested that the increase in stability is the result of a reversible structural change in the adsorbed layers on the rubber particles

The mechanical stability time (MST) of a natural latex concentrate is known to increase markedly during the first three months after centrifugation and it is also known that the storage temperature during this period is important in determining the stability increase. However, once a latex concentrate is three months old, its MST becomes relatively constant and tends to change very little on prolonged storage. It is surprising, therefore, to observe a significant increase in the MST of mature concentrates after a short period of heating at e.g. 60°C. In the present work, the effect of varying the conditions of heat treatment on MST and the effects of heat treatment on other latex properties were investigated in an attempt to find the cause of the phenomenon.

EXPERIMENTAL

The latex concentrates used in these experiments, with the exception of LATZ.2 (the suffix number indicates the sample used), were samples of commercial concentrates imported into the UK in the period 1987-89 and were not less than three months old. The LATZ 2 latex was specially air-mailed to the UK soon after concentration and was only two weeks old at the time of the test.

Mechanical stability tests were carried out in accordance with the international test method (ISO 35) at a temperature of 35°C. The zinc

oxide mechanical stability test (ZST) was the 'German' method¹ and the viscosity increase test (ZAAV) was that described by Gorton and Pendle². The KOH numbers referred to in the paper were obtained by the conductimetric titration method of Gorton and Pendle³ but the VFA numbers, alkalinity values, zinc and nitrogen contents and viscosities were all determined by the appropriate ISO test methods.

Latex particle size measurements were carried out by photon correlation spectroscopy using a Malvern 4600 instrument⁴. Each result quoted is the average of ten measurements. The electrophoresis measurements were carried out using an apparatus similar to that described by Blackley and Charnock⁵. The mobile phase was latex diluted to 10% TSC with de-ionised water and the stationary phase was a glycine/sodium chloride/sodium hydroxide buffer solution at the same specific conductivity and pH as the mobile phase. The measurements were made at 25°C.

Measurements of fatty acids were made using the cold extraction method of Chen and Ng⁶ followed by methylation/gas chromatography using heptanoic acid as the internal standard. Latex serum anions were determined by ion-chromatography as previously described⁷. Measurements of specific surface area were carried out by the method described by Chen⁸.

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Measurements of gelling pH and gelling time were carried out at a fixed temperature (25°C) and fixed d.r.c. value (58.0%) by adding 0.8 weight percent of sodium silicofluoride on the weight of rubber.

Low temperature treatments of latex samples were carried out by placing 200 ml of latex in a sealed, screw top, 250 ml bottle in a refrigerator at 4°C for three days or in a freezer at -23°C for 16 h. In both cases, the sample bottles were allowed to return to room temperature naturally. Latex heating experiments were carried out by placing *ca.* 200 g of latex in a 250 ml screw-top polythene bottle, replacing the bottle cap then standing the bottle in a hot-water bath at the required temperature. After the designated heating time, the bottle was removed from the bath and allowed to cool to room temperature ($\sim 23^\circ\text{C}$) naturally. If not otherwise specified, the term, 'heat treatment' refers to conditions of 60°C for 30 min. (The

temperatures quoted are those of the water bath, refrigerator, *etc.* and only in the longer duration experiments are these the same as the temperature of the latex samples. Under the conditions in use in these experiments, the latex samples reached the temperature of the bath after approximately 30 min immersion.)

RESULTS AND DISCUSSION

When it was found, in the course of our studies of the stability behaviour of natural latex, that a short period of heating at 70°C could significantly increase the mechanical stability of latex, it was decided that this phenomenon merited further investigation. Firstly, it was decided to establish the range of heat treatments that would produce a stability increase. Therefore, the effect on the stability of samples of latex of heating for 15 min at a range of temperatures was investigated. The results of these tests are shown graphically in *Figure 1*.

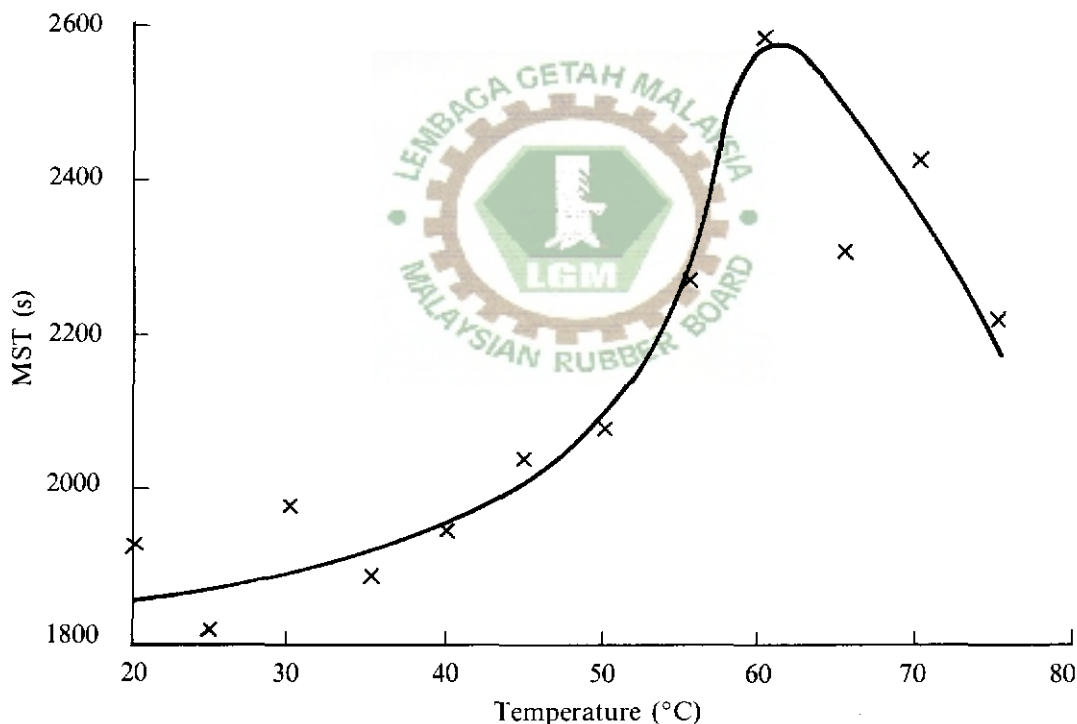


Figure 1. Mechanical stability time of HA. 2 latex as a function of temperature of heat treatment.

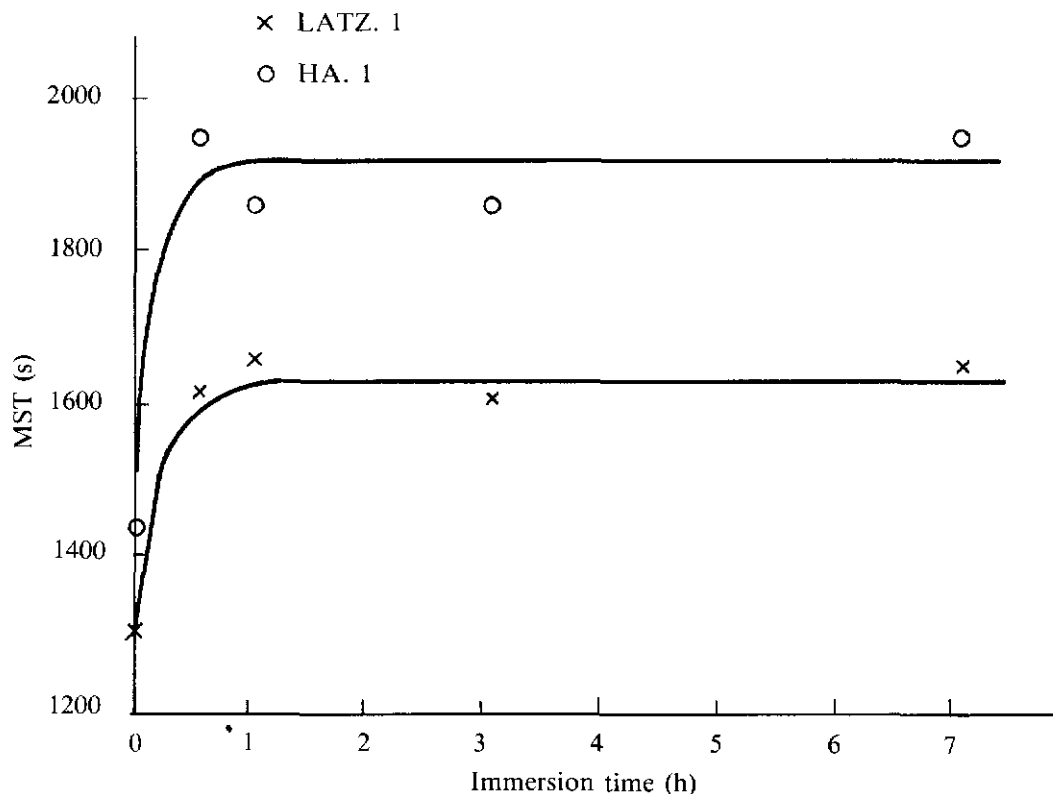


Figure 2. Mechanical stability time of latex as a function of duration of heating.

From these results, it is clear that no increase in mechanical stability is obtained at temperatures below 45°C and that the maximum stability increase occurs at about 60°C. The effect of duration of heating was then examined by heating latices at 60°C for various periods. The results obtained with two latices are shown in Figure 2. From these data, the optimum duration of heating, at 60°C, is 30–60 min and it is clear that prolongation of heating (up to 7 h) has little further effect.

To determine whether the induced stability increase was a permanent effect, two latices that had been heat-treated were stored at room temperature for up to 200 days. Control samples of the same latices were simultaneously stored under the same conditions. At the end of this period, the mechanical stabilities of the heat-treated samples were not greatly different from those of the control samples (Table 1), since the mechanical stabilities of the control samples increased much more during storage.

TABLE 1. MECHANICAL STABILITY CHANGES ON STORAGE IN AIR

Storage time (days)	Mechanical stability changes (ratios to initial control values)			
	HA. 1		LATZ. 1	
	Control	Heated	Control	Heated
0	1.00	1.35	1.00	1.25
200	1.91	1.83	1.62	1.68

The results were essentially the same when the air above the surface of the latex was replaced with nitrogen (*Table 2*), thus suggesting that

the MST increase was not related to the well-known phenomenon of increased stability due to exposure to oxygen⁹. Further evidence of

TABLE 2. MECHANICAL STABILITY CHANGES ON STORAGE UNDER NITROGEN

Storage time (days)	Mechanical stability changes (ratios to initial control values)			
	HA. 1		LATZ. 1	
	Control	Heated	Control	Heated
0	1.00	1.26	1.00	1.22
200	1.85	1.64	1.48	1.52

this was given by the results of experiments in which the air over the latex was replaced by nitrogen during the heat treatment itself (*Table 3*).

TABLE 3. INFLUENCE OF AIR AND NITROGEN ON HEAT-TREATMENT EFFECT

Latex sample	Gas over latex sample	MST (s)
HA. 1	Air	2 240
HA. 1	Nitrogen	2 210
LATZ. 1	Air	1 610
LATZ. 1	Nitrogen	1 600

These results suggest that the heat treatment may simply be accelerating a change that would otherwise have occurred naturally on prolonged storage. If this were the case, some relation to the changes presumed to take place when a fresh latex concentrate matures might be expected. Also, the extent of change in stability on heating would be expected to be greater in a freshly-made concentrate than in an older one.

This possibility was examined by comparing the effect of heating on two concentrates, one only two weeks old and the other three years old. The results are given in *Table 4* and show that the 'young' concentrate increased in stability much more than the older one. This, again, suggest that the heat treatment is in effect producing an accelerated maturation of the latex.

The traditional view of the increase in mechanical stability of a fresh NR latex concentrate on storage is that it arises through hydrolysis of lipids with the consequent production of fatty acid soaps. To investigate whether this short period of heating did produce any detectable change in the fatty acid content of a latex, a comparison was carried out on a HA latex. The results are presented in *Table 5*. It is concluded that no significant difference is detectable between the heated sample and the control. The rise in the mechanical stability of a latex could be due to an increase in the ionic charge on the particles, due to the production of soaps or other ionic species, and this possibility was examined by two independent methods. Electrophoretic mobility measurements were carried out (*Table 6*) and measurements

TABLE 4. INFLUENCE OF AGE OF LATEX ON THE RESULTS OF HEAT TREATMENT

Latex	Age	MST(s)		Relative MST heat treatment
		Normal	Heat treated	
LATZ. 2	2 weeks	420	840	2.0
LATZ. 3	3 years	1 125	1 245	1.11

TABLE 5. EFFECT OF HEAT TREATMENT ON HIGHER FATTY ACID CONTENT (HA. 6 Latex)

Fatty acid	Concentration (mg/100g latex)	
	Control	Heated
C12	34	35
C14	2	1
C16	32	31
C16:1	2	2
C18	70	72
C18:1	67	69
C18:2	173	183
C18:3	13	14
C20	4	5
Furanoate	9	3
Total	406	415

TABLE 6. EFFECT OF HEAT TREATMENT ON ELECTROPHORETIC MOBILITY

Latex sample	Electrophoretic mobility ($10^{-8} \text{ m}^2 \cdot \text{v}^{-1} \cdot \text{s}^{-1}$)	
	Control	Heated
HA. 2	6.3	6.1
LATZ. 4	6.2	6.4
HA. 5	6.4	6.3

TABLE 7. EFFECT OF HEAT TREATMENT ON CONDUCTIMETRIC KOH TITRES (HA. 2 Latex)

Latex/serum	KOH titres (mmoles KOH/100g rubber)	
	Control	Heated
Latex	17.16	17.00
Serum	13.97	13.97
(Latex-serum)	3.19	3.02

of the total ammonium ion concentrations present in the latex and the serum were also made (*Table 7*). Neither of these methods revealed any significant change due to the heat treatment.

The failure to find evidence of changes in the absorbed surface ions after heat treatment made it necessary to look for alternative explanations. A wider range of latex properties and characteristics was therefore examined for evidence of change due to heat treatment. *Table 8* shows the effects of heat treatment on the zinc stability characteristics of two latices. It can be seen that the zinc oxide mechanical stability values increase, as would be expected, in parallel with the MST values whereas the zinc-ion viscosity stability behaviour (ZAAV value) is essentially unaffected.

The average particle size values of a number of latices were measured before and after heat treatment (*Table 9*) because a change in particle size could conceivably produce a change in mechanical stability. Once again, however, no significant change was detectable.

The concentration and nature of ions in the serum of a latex may play a part in determining its stability and it was therefore decided to analyse the serum anions of a latex before and after the heat treatment. The results of these measurements are given in *Table 10* and indicate no significant change in the total anion concentration or in the concentrations of individual anions. The absence of change in the total anion concentration is consistent with the results obtained by KOH titration of the serum of the same latex (*Table 7*).

Recent work in this laboratory has shown that the quantity of zinc associated with the rubber phase of a latex influences its stability,

TABLE 8. EFFECT OF HEAT TREATMENT ON ZST AND ZAAV VALUES

Latex sample	ZST value(s)		ZST/MST ratio		ZAAV ratio	
	Control	Heated	Control	Heated	Control	Heated
HA. 2	405	455	0.21	0.18	1.2	1.3
LATZ. 4	330	420	0.37	0.36	1.3	1.5

TABLE 9 EFFECT OF HEAT TREATMENT ON LATEX PARTICLE SIZE

Latex sample	Z Average diameter (nm)	
	Control	Heated
HA 3	614	642
HA 4	553	596
LATZ 1	533	532
LATZ 5	527	533
LATZ 6	536	564

TABLE 10 EFFECT OF HEAT TREATMENT ON SERUM ANION CONCENTRATIONS (HA 2 Latex)

Anion	Concentration (mmol dm ⁻³)	
	Control	Heated
Citrate	16.8	17.7
Acetate	15.3	15.9
Malate	13.4	13.3
Succinate	4.83	5.08
α Glycerophosphate	4.44	4.34
β Glycerophosphate	2.32	2.28
Oxalate	1.45	1.34
Formate	1.40	1.53
Phosphate	0.97	0.86
Sulphate	0.95	1.05
Chloride	0.68	0.68
Total	62.54	64.06

this phenomenon will be discussed in a later publication, measurements were therefore made of the distribution of zinc in a LATZ latex

TABLE 11 EFFECT OF HEAT TREATMENT ON THE DISTRIBUTION OF ZINC (LATZ 1 Latex)

Phase	Zinc content ($\mu\text{g/g latex}$)	
	Control	Heated
Rubber	121.7	117.1
Serum	82.9	81.0
Sediment	5.9	3.2
Total	210.5	201.3

before and after heat treatment. The results, shown in *Table 11*, indicate no significant change.

With the exception of the MST and ZST values, no other characteristic of the latex has been found to change significantly as a result of heat treatment, including all of the factors likely to affect colloidal stability. To confirm this conclusion, a further range of latex properties were determined before and after heat treatment. The properties measured and the results obtained are shown in *Table 12*. In no case was any effect of heat treatment detected.

The absence of any evidence of chemical or physical changes (other than MST and ZST) after heat treatment suggested that the stability rise could possibly be a consequence of a thermally induced *structural* change in the adsorbed layer at the particle surface. This in turn, suggested that the reverse effect might occur if the latex were cooled. In consequence, experiments were carried out on three latices to

TABLE 12 EFFECT OF HEAT TREATMENT ON VARIOUS LATEX PROPERTIES

Property	Latex	Control	Heated
Viscosity (cP)	HA 2	95	95
pH of gelation	LATZ 4	7.38	7.28
Gelling time (s)	LATZ 4	108	113
Alkalinity (%)	LATZ 1	0.19	0.21
VFA number	LATZ 1	0.04	0.04
Surface nitrogen (mg/g latex)	HA 2	1.69	1.65
Specific surface area (m ² /cc rubber)	LATZ 1	11.1	11.1

assess whether cooling them would reduce their mechanical stability values. In addition, after cooling to low temperatures and returning to room temperature, samples of the latices were subsequently heat-treated to determine whether an increase in MST could still be obtained. The results of these measurements are given in *Table 13*. It is clear that cooling, even at temperatures well above freezing, does reduce the MST values (measured at 35°C) but that the effect is quite reversible because subsequent heat treatment produces a substantial increase.

Table 14 shows that even the effect of freezing can be partially reversed by subsequent heating although the degree of reversal varies among different latices.

TABLE 13. EFFECT OF COOLING AND HEATING ON THE MECHANICAL STABILITY OF LATICES

Cooling/heating	MST(s)	
	HA. 7	LATZ. 7
Control	1 215	960
Heated	1 470	1 095
Cooled	1 130	900
Cooled then heated	1 405	1 100
Heated then cooled	1 430	1 095

The heat-treatment effect itself is not substantially reversed by subsequent freezing. Again, the degree of reversal depends on the particular latex tested.

TABLE 14. EFFECT OF FREEZING AND HEATING ON THE MECHANICAL STABILITY OF LATICES

Freezing/heating	MST (s)		
	LATZ. 1	HA. 7	LATZ. 7
Control	1 275	1 215	960
Heated	1 600	1 470	1 095
Frozen	980	630	180
Frozen then heated	1 370	880	295
Heated then frozen	1 530	930	310

CONCLUSION

Heating natural latex concentrates, of almost any age, to 60°C produces significant increases in mechanical stability which are not due to changes in the quantity or nature of the adsorbed or serum ions, and are not due to a particle size change. The changes appear to be purely thermally induced and to be at least partially reversible.

It is suggested that the mechanical stability increase may be due to a reversible change in the structural configuration of the adsorbed surface layer, possibly in the adsorbed protein, but there is no direct experimental confirmation of this idea.

The fact that the thermally induced MST increase appears to be an acceleration of the effect of long-term storage suggests in turn that the MST rise observed as latex concentrates mature may not be solely due to the hydrolysis of lipids. This conclusion has also been reached by Hasma¹⁰ on the basis of other evidence.

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