Proceedings of Placrosym XV (2002): 643-649

EVALUATION OF SALT ACID MIXTURE AS COAGULANT OF LATEX FOR SHEET PRODUCTION

Rosamma Alex, C.K. Premalatha and Baby Kuriakose
RRII, Kottayam, Kerala - 686 009

ABSTRACT

Rubber is recovered from natural rubber latex by coagulating it with coagulants like formic, sulphuric and solphamic acids. In order to find out the feasibility of using other less expensive and commonly available materials, a study has been conducted using a combination of formic acid, sodium chloride and calcium chloride which are no known to have some coagulant properties. The studies revealed that a coagulant mixture consisting of a combination of these salts and formic acid is a cheaper substitute for the currently used formic acid. This mixture did not cause any adverse effect on raw rubber properties, cure behaviour, ageing characteristics and development of mould growth. Further, the coagulant mixture gave a firmer coagulation with reduced time of sheeting and a serum of higher pH.

INTRODUCTION

Rubber is recovered from natural rubber (NR) latex by coagulating it with a suitable coagulant followed by processing of the coagulum. For coagulating latex, acetic, formic sulphuric (Wiltshire, 1932; Martin *et al.*, 1934; George *et al.*, 1990) and sulphamic acids (Sebastian *et al.*, 1982) are generally used. In addition, there are practices of assisted biological coagulation (John, 1966) and autocoagulation for separation of rubber from latex. Formic acid which is an ideal coagulant is costly whereas sulphuric acid is slow as compared with formic acid. The raw rubber properties obtained by autocoagulation is poor. Hence, it will be useful to identify a coagulant which is as effective as formic acid, more economical and having less adverse effect on the properties of rubber.

The coagulants generally bring about coagulation by removing the protein layer surrounding rubber particles. A substance which generates hydrogen ions in the aqueous phase brings about reduction in the colloidal stability, by reducing electric charge density together with concomitant surface potential by chemical reactions. Salts which are neutral like NaCl reduce colloidal stability by compressing electrical double layer, by increasing the ionic strength of the aqueous phase. Salts of cations of higher valency like calcium destabilize latex by loss of surface bound electric charge due to chemical reaction. Sodium and calcium salts have no pro-oxidant action and are not hazardous. Moreover, they are easily available and cheap. Hence, a combination of formic acid, sodium chloride and calcium chloride is expected to act as cheap coagulant for latex in preparation of sheets. There are many reports (John, 1971; John, 1976) on quick coagulation of latex by addition of calcium chloride and anionic surfactant for the preparation of crumb rubber. However, they have never been tried as coagulants for sheet preparation. The present work is an attempt to identify an effective and cheap coagulant, from an appropriate combination of metal salts and formic acid.

MATERIALS AND METHODS

Formic acid, sodium chloride and calcium chloride were the chemicals used for the preparation of coagulant mixture. These were of laboratory grade and purchased from local sources.

Preparation of coagulant mixture

Calcium chloride and sodium chloride were weighed as per the formulation given in Table 1, dissolved in minimum quantity of water, added formic acid and made up to 1 litre with water. 25 ml of this, mixture after diluting to 250 ml, was used for coagulation of field latex containing 500g dry rubber. For comparison, formic acid was used as the standard coagulant. Rubber sheets were prepared by following standard procedure using the required quantity of chemicals. Effectiveness of the coagulant was evaluated by the following observations.

1. Quality of serum as assessed by visual observation and by measurement of suspended solids of serum.
2. Quality of coagulum as determined from firmness of coagulum, visual observation on colour/frothing and for the easiness in sheeting of the coagulum.

3. Time for complete coagulation as assessed by observing the time for maturation of coagulum which is ready to the level of sheeting.
4. Rate of drying of sheets as assessed by weighing the sheets at definite time intervals.
5. Time for complete drying and
6. Recovery of rubber by weighing the final sheet.

The metal salts retained on the rubber sheet was estimated using spectrophotometry, for calcium and magnesium. Quality of sheets was assessed by visual grading as well as by measurement of raw rubber properties by standard test methods. Analysis of the serum for parameters such as BOD, COD, pH, calcium ions, chloride ions, suspended solids and dissolved solids was also conducted by following standard test procedures. The cure characteristics were assessed by ACSI mixes and the technical properties were evaluated by standard carbon black filled mixes as per ASTM D 3184-89. Accelerated ageing tests were carried out by measurement of the technical properties such as tensile strength, modulus and elongation at break after ageing at 70° C for 96 h. The storage quality of sheets was assessed by measurement of moisture content and development of fungus growth by visual observation.

Table 1. Formulation of 1 liter of coagulant mixture

Chemicals	Quantity
$CaCl_2, 2H_2O$	120 g
NaCl	60 g
Formic acid	548 ml
Water	As required to make up to 1 liter

RESULTS AND DISCUSSION

A. Effect on sheet processing characteristics

(1) Effect on pH of coagulation, nature of coagulum and maturation time

Coagulation of latex for preparation of sheets is expected to take place, after a certain time delay during which latex gets converted to a uniform and smooth coagulum. This is possible by precipitation of the protein layer around the rubber particles in the pH range 4.4 - 4.8 (Kuriakose, 1992; Pries, 1970). The coagulation characteristics of the coagulant mixture as compared with formic acid is given in Tables 2 and 3. The pH of coagulation for coagulant mixture was around 4.8 whereas that of formic acid was around 4.6. The coagulant mixture gave a firmer coagulum in a shorter time, and a rubber recovery similar to that obtained using formic acid.

(2) Effect of pH of serum

The pH of serum from latex coagulated with the new coagulant mixture was higher than that using formic acid. It is advantageous to have a higher serum pH so as to reduce environmental problems due to higher acidity. The serum clarity using the two coagulants is given in Figure 1. The slight turbidity of coagulant mixture is shown to be due to formation of insoluble calcium soaps in the serum.

Fig. 1. Photograph of serum obtained after coagulation of latex with coagulant mixture (sample) and formic acid (control)

(3) Effect of drying time

The rate of drying for sheets prepared using coagulant mixture is the same as that by using formic acid (Fig. 2). As the coagulant mixture contained salts, the coagulum was more matured as compared to acid coagulation, because destabilization of latex was by precipitation of proteins and also by compression of electrical double layer due to increased ionic strength. In the case of sheets prepared from coagulum of same hardness, drying time did not vary by using either

Table 2. pH of coagulation of latex of two different dilutions using coagulant mixture and formic acid

Dilution of latex based on DRC%	pH of coagulation	
	Coagulant mixture	Formic acid
18	4.47	4.34
12	4.80	4.61

Table 3. Coagulation characteristics of coagulant mixture as compared with formic acid

Parameters	Formic acid	Coagulant mixture
Minimum coagulation time required for sheeting the coagulum	> 7 hours	4-5 hours
Clarity of serum	Clear serum	Almost like control
PH or serum	4.7	5.1
Recovery of rubber	570 g	570 g
Drying time	4 days	4 days

coagulant mixture or formic acid. However, for sheets prepared on next day a higher thickness was observed due to over maturation of coagulum where the coagulant mixture was used.

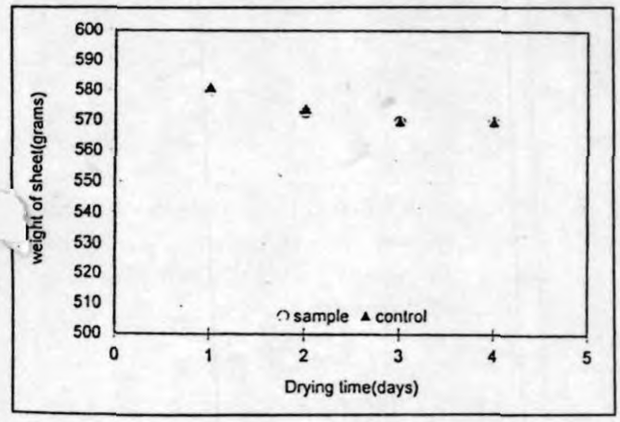

Fig. 2. Rate of drying of the sheets preparted using coagulant mixture (sample) and formic acid (control)

(4) Effect on effluent

The effluent characteristics of the serum are given in Table 4. The serum from the coagulant mixture contained a comparatively higher amount of dissolved solids (DS) calcium and chloride, as the coagulant mixture was composed of soluble salts. It appeared that the salts were not retained on the rubber sheet but transferred to the rubber serum during coagulation. As will be seen later, the ash content was not significantly affected by use of coagulant mixture. Due to this reason chemical oxygen demand (COD), biological oxygen demand (BOD) and suspended solids (SS) were also marginally higher for serum from coagulant mixture. There was no significant difference for the presence of sulphite in the serum. The effective values of these parameters in the effluent would be much reduced as the actual effluent would include the water used during the various processing operations which was estimated to be approximately 20 L of water per kg of processed ribbed smoked sheet (Thomas *et al.*, 1980).

(5) Effect on storage quality

The mould growth was low and comparable for both formic acid and coagulant mixture. The fungus growth increases in the presence of moisture retained on rubber sheets. As no significant levels of salts were retained on rubber sheets prepared using coagulant mixture there was no moisture, absorption during storage of sheets.

(6) Cost consideration

The cost advantage obtained by using coagulant mixture is given in Table 5. The expected saving in cost of coagulant is Rs.72.85 per metric ton of processed sheets.

Table 4. The effluent characteristics of rubber latex serum prepared using coagulant mixute and formic acid

Parameters	Formic acid	Coagulant Mixture
COD, mg/1	4940	5610
BPD, mg/1	3420	4290
Dissolved solids, mg/1	5650	6350
Suspended solids, mg/1	250	260
Calcium, mg/1	6.4	182
Sulphite, mg/1	17.6	35.2
Chloride, mg/1	trace	570

B. Effect of Raw rubber properties

The variation in raw rubber properties of the rubber sheets analysed statistically are given in Tables 6, a, b & c. The acetone extractables (that contain the fatty acids, lipids etc) and nitrogen content of rubber sheets prepared using coagulant mixture (sample) was to a small extent lower than that for formic acid (control) coagulated sample but in the normal range obtained for sheets (Sapronov *et al.*, 1975). There was a difference between the coagulants for level of calcium retained on sheets but is insignificantly low, as this did not effect the rate of drying of sheets, development of mould growth and on the resistance to oxidative degradation as will be seen later. The rubber sheets prepared using formic acid was sheeted out after a longer time as compared with coagulant mixture, which favour crosslinking reactions involving rubber molecules and nitrogenous or oxygen containing groups present in non-rubber constituents thus increasing the amount of acetone extractable materials trapped with rubber during coagulation. As a consequence of this, the nitrogen content, which is a measure of proteins, also increased for the sheets prepared using formic acid. The dirt content was not affected by the type of coagulant as this parameter has a bearing only on the method of preparation. The values obtained were low and in the range observed earlier (Nair, 1975). The mean value of initial plasticity (P_0) for both the control were comparable, even though there was a significant statistical variation between the coagulants. However, aged plasticity (P_{30}) and the resistance to oxidative degradation as measured by PRI showed no statistical variations and were comparable for sheets from the coagulant mixture and formic acid. It is well known that PRI is adversely affected only by metallic contaminants like Cu, Mn, Fe or over maturation of coagulum and not by the method of coagulation.

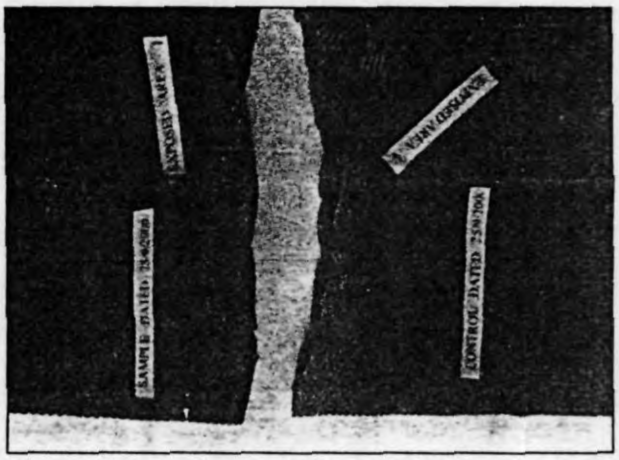

Fig. 3. Photograph of fungus growth on rubber sheets stored for six months prepared using coagulant mixture (sample) and forr^ic acid (control)

C. Cure behaviour of ACSI mixes

The rate and degree of vulcanization of the ACSI mix (Table 7) remained at a similar level for sheets prepared using coagulant mixture and formic acid as indicated by the scorch time, torque maximum, torque minimum, cure rate index and optimum cure time given in Table 8. Generally, the cure behaviour is affected by factors like pH of coagulation (Alias *et al.*, 1980; Loke, 1991) maturation of coagulum and fatty acids retained on sheets (Jayasuriya *et al.*, 2000; Hoffman, 1967). As the values of these parameters were very close in the case of the sample and control the results obtained showed almost the same cure behaviour.

Table 5. Cost of coagulants

Parameters	formic acid: coagulum sheeted after about 7 h (conventional	Formic acid: coagulum sheeted after about 4 h	Coagulant mixture coagulum sheeted after about 4 h
Coagulant required for production of 1 kg of Sheet rubber	4 cc (4.82 g)	4.4 c (5.302 g)	11.81 g
Cost of coagulant for production of 1 kg of sheet rubber	Paise 25.06	27.57	20.28
Cost of coagulant for production of 1 MT of sheet rubber	Rs.250.64	Rs.275.70	Rs.202.85

Table 6. Raw rubber Properties

a. Ash analysis

Statistical parameters	Ash content		% calcium		% magnesium	
	Sample	Control	Sample	Control	Sample	Control
Mean	0.26	0.26	0.26	0.00093	0.022	0.023
SD	0.33	0.01	0.0047	0.00016	0.0025	-0.001
T Value	-0.22		-18.74		132	
Variation	NS		S		NS	

b. Volatile matter, dirt content, acetone extractables and nitrogen

Statistical parameters	Volatile matter		Dirt content		Acetone extractables		Nitrogen	
	Sample	Control	Sample	Control	Sample	Control	Sample	Control
Mean	0.67	0.71	0.012	0.011	2.68	2.83	0.37	0.43
SD	0.086	0.1	0.004	0.003	0.08	0.16	0.034	0.041
T Value	2.407		1.1		4.28		6.90	
Variation	NS		S		NS		S	

c. P_0, P_{30} and PRI

Statistical parameters	P_0		P_{30}		PRI	
	Sample	Control	Sample	Control	Sample	Control
Mean	46.75	46.33	35.25	35.75	76	77
SD	4.51	3.98	3.49	3.33	4.98	4.26
T Value	3.45		0.59		1.33	
Variation	S		NS		NS	

D. Black filled compound

The physical properties of carbon black filled mixes in a standard formulation (Table 9) are given in Table 10. As seen ,the technical properties like the tensile strength, tear strength, resilience, compression set and heat build-up of the sheets prepared using coagulant mixture had comparable properties to that prepared using formic acid.

E. Ageing characteristics

The physical properties of carbon black filled vulcanizates after ageing at 70°C for 96 hrs are given in Table 11. The ageing characteristics of the sheets prepared using coagulant mixture were similar to that of the formic acid coagulated sheets.

Table 7. Formulation of ACSI mixes

Ingredient	Parts by weight
Natural rubber	100
ZnO	6
Stearic acid	0.5
MBT	0.5
Sulphur	3.5

Table 8. Cure characteristics of ACSI mix

Statistical parameters	Scorch time, mintures		Torque maximum, dN.m		Torque minimum dN. m		Optimum cure time at 150°C, minutes		Cure rate index min^{-1}	
	Sample	Control	Sample	Control	Sample	Control	Sample	Control	Sample	Control
Mean	3.85	3.67	38.08	36.63	6.04	5.81	21.31	21.44	0.98	0.94
SD	0.41	0.46	2.82	4.09	0.70	1.23	1.86	2.34	0.12	0.17
T Value	-1.32		-2.08		-0.57		0.318		-1.25	
Variation	NS		NS		NS		NS		NS	

Table 9. Formulation of standard carbon black filled compound as per ASTM D3184-89

Ingredient	Parts by weight
Natural rubber	100
ZnO	5
HAF black	35
Stearic acid	2
CBS	0.7
Sulphur	2.25

Table 10. Physical properties of carbon black filled mixes

Parameters	Sample	Control
Tensile strength, MPa	31.03	30.16
Modulus 300%, MPa	13.14	13.14
Elongation at break, %	540	520
Tear strength kN/m	76	79
Heat build up, T°C	17	17
Compression set, %	22	22
Rebound resilience, %	61	60
Hardness, Shore A	55	54

Table 11. Ageing characteristics

Parameters	Sample	Control
Modulus 300%, MPa	14.35	14.45
Tensile strength, MPa	27.3	28.3
Elongation at break, %	500	500

CONCLUSION

A coagulant mixture consisting of a combination of salts and formic acid is a cheap substitute for the currently used formic acid as a coagulant for NR latex with no adverse effect on raw rubber properties, cure behaviour, ageing characteristics and development of mould growth. In addition, the coagulant mixture gave a firmer coagulum with a reduced time of sheeting and a serum of higher pH.

REFERENCES

Alias Bin Othman and Chan Boon Lye. 1980. 'Effect of pH of coagulation and sulphuric acid as a coagulant on natural rubber properties'. *Journal of Rubber Research Institute of Malaysia, 28(3), p. 109-118*

George, K.M., Varghese, L. and Mathew, N.M. 1990. 'Use of sulphuric acid as coagulant for natural rubber latex'. *Proceedings of the Ninth Symposium on Plantation Crops*, PLACROSYM IX, Bangalore, p. 336-341

Hoffman, W. 1967. 'Vulcanisation and vulcanizing agent'. London : Maclerene and Sons Ltd., p 151-153

Jayasuriya, M.M., Mithrananda, K.M.U., Yapa, S., Ratnayake, U., Siriwardena, S., Kumara, G., Liyanage, R., Kurupu, C. and Wejesekara, M. 2000. 'Effect of drying conditions on the technological properties of sheet natural rubber'. *Journal of Rubber Research*, 3(3) p. 185-192

John, C.K. 1966 'Biological coagulation of Hevea latex using waste carbohydrate substrates' *Journal of Rubber Research Institute of Malaya*, 19(5) p. 286-289

John, C.K. 1971. 'Coagulation of *Hevea* latex with surfactant and salt: 1. Development of the process and its effect on raw rubber properties. *Journal of Rubber Research Institute of Malaysia*, 23(2) p. 147-156

John, C.K. 1976. 'Coagulation of *Hevea* latex with surfactant and salt II, Batch-wise commercial processing'. *Journal of Rubber Research Institute of Malaysia*, 24(3) p. 125-130

Kuriakose, Baby 1992. 'Primary processing' In: Natural Rubber : Biology, Cultivation and Technology. Ed. M.R. Sethuraj and N.M. Mathew. Elseiver publications p. 382-386

Loke, K.M. 1991. 'Rivisions to SMR scheme'. *Proceeds of Rubber Growers Conference*, Kuala Lumpur, p 511-534

Martin, G. and Davey, W.S. 1934. 'Rubber from latex coagulated with sulphuric acid'. *Journal of Rubber Research Institute of Malaya*, 5, p. 282-294

Nair, S. 1975. 'A decade of Standard Malaysian Rubber'. *International Rubber Conference, Proceedings*, V, p.343-363

Pries. O.S. 1970. 'Ribbed Smoked Sheets'. *In:* A handbook of rubber culture and processing, Rubber Research Institute of Ceylon, p. 119-141

Thomas E.V., M.G. Kumaran and Kothandaraman, R. 1980. 'Collection and processing of crop'. *In:* A Hand book of Natural Rubber Production, Rubber Research Institute of India, p. 337-357

Sapronov, V. and Emeljanov, D. 1975. 'Comparative evaluation of some types of natural rubber'. *International Rubber Conference, Proceedings*, V, p. 407-430

Sebastian, M.S., Balan, M.V. and Thomas, E.V. 1982. 'A new coagulant for natural rubber latex'. *Proceedings of the fifth Annual Symposium on Plantation Crops*, PLACROSYM V, P. 316-323

Wiltshire, J.L. 1932. 'Sulphuric acid as a latex coagulant'. *Journal of Rubber Research Institute of Malaya*, 4(2) p.94-103

* * *