

Accelerated Auto-coagulation of Skim Latex

C. K. JOHN and SIN SIEW WENG

An economic and practical method of coagulating partially de-ammoniated skim latex by the addition of 0.1% dioctyl sodium sulphosuccinate and 1.0% calcium chloride is described, in which the coagulation time is reduced to two days from the five days required for spontaneous coagulation. The resulting rubber is much less smelly and its technological properties superior to that made from auto-coagulated or acid-coagulated skim, with improved scorch time, PRI and resilience and reduced hardness, modulus and heat build-up.

When latex is centrifuged it separates into approximately equal volume of concentrate latex containing about 60% d.r.c. and skim containing about 4-8% d.r.c. Rubber is normally recovered from skim by coagulating with sulphuric acid. It contains 70-85% rubber hydrocarbon, 5-10% acetone-soluble fatty materials and 10-20% protein, compared with an average of 95% hydrocarbon, 3% fatty materials and 2% proteins for smoked sheet prepared from field latex (MORRIS, 1954). Consequently, the technological properties of skim rubber are quite abnormal, notably its proneness to scorch (BAKER, 1958). Many attempts have been made in the past to improve the properties of skim rubber. MORRIS (1954) and BARNWELL (1957) successfully decomposed the protein by enzymic deproteinisation, bringing about considerable improvement in the technological properties. FIRESTONE TYRE AND RUBBER COMPANY (1955) achieved the same result by treating spontaneously-coagulated skim coagulum with an aqueous metal hydroxide solution. BAKER (1958) showed that skim rubber can be used with advantage if proper compounding is carried out.

In the production of new types of block rubber, skim latex (de-ammoniated to < 0.1% ammonia) is spontaneously coagulated and the coagulum granulated and pelletised. The resulting block skim rubber is far superior in its properties to acid-coagulated skim

rubber (SMITH, 1969). The drawbacks of this method, however, are that it takes four to five days to complete the coagulation, requiring extensive coagulation-tank capacity to handle large quantities of skim and that the resulting coagulum and dry rubber are foul smelling.

JOHN (1966a) showed that auto-coagulation of field latex can be accelerated by increasing the carbohydrate content available for microbial breakdown. Coagulation time can be further reduced by adding an anionic surfactant (JOHN AND PILLAI, 1971), an instant coagulation being obtained in the combined presence of the surfactant and calcium chloride (JOHN, 1971). This paper describes the application of the surfactant + salt (i.e. calcium chloride) coagulation method to skim.

MATERIALS AND METHODS

Skim

Freshly collected skim latex containing about 0.4% ammonia (pH about 10) and an initial bacterial population of approximately 10^8 cells per millilitre was used. Its d.r.c. varied from 3.5 to 5.0% depending on the efficiency of centrifugation.

Additives

The additives used were molasses (containing about 50% sugar), Aerosol GPG, calcium

chloride and sulphuric acid. Aerosol GPG is a 75% solution of dioctyl sodium sulphosuccinate in a water/alcohol mixture; when not otherwise specified this material is referred to as the surfactant. Three grades of calcium chloride were used: dried analar, fused porous lump and commercial grade lump. All additions were made on the basis of the d.r.c. of the skim, except sulphuric acid which was used at 5% concentration to bring the pH to 4. Both calcium chloride and molasses were added as a 50% solution in water and the surfactant as a 10% solution. When surfactant and calcium chloride were used in the same system, the surfactant was added first, followed by the salt, with adequate stirring between the two additions.

De-ammoniation

Separate methods were adopted for de-ammoniation of small and large quantities of skim. For small quantities, air was passed through the skim while stirring but for large quantities, the skim was pumped up to a tower and allowed to slowly trickle down while air was simultaneously blown up. This operation was repeated until the ammonia content was reduced to 0.1% or below.

Processing of Coagulum

The coagulum was either granulated or crumbled; the former was achieved by cutting the coagulum manually into 1 ft cubes and feeding them into a granulator to obtain small pellets (SMITH, 1969), the latter by making the coagulum into a thick crepe, passing it through a pair of rollers to smear it with castor oil (0.7% on d.r.c.) and then crumbling it (SEKHAR *et al.*, 1965).

RESULTS

Effect of Surfactant and Molasses on Coagulation

De-ammoniated skim containing 0.5% ammonia was treated in 1-gal aliquots with two levels of surfactant (0.1 and 0.2%) and

TABLE 1. COAGULATION OF SKIM LATEX WITH MOLASSES AND SURFACTANT

Molasses (%)	Surfactant (%)	Coagulation efficiency* after 60 h
—	0.00	+
—	0.10	++
—	0.20	+++
2.5	0.00	++
2.5	0.10	+++
2.5	0.20	++++
5.0	0.00	+++
5.0	0.10	+++++
5.0	0.20	+++++

*Estimated visually with a scoring system of 1–6

of molasses (2.5 and 5.0%) and allowed to coagulate. The coagulation efficiency was observed after 60 h (*Table 1*).

As the concentration of molasses was increased the coagulation efficiency improved, but even with 5% molasses complete coagulation was not obtained even after two-and-a-half days. In the added presence of the surfactant a more complete coagulation was observed, with reasonable efficiency at 5% molasses and 0.2% surfactant; however, these levels are considered uneconomically high.

Effect of Surfactant and Calcium Chloride on Coagulation

Skim latex de-ammoniated to about 0.06% (pH 8.75) was treated in quantities of 15 gal with 0.1% surfactant and 0.5%, 0.75%, 1% or 2% commercial calcium chloride. The coagulation efficiency was observed after 48 h (*Table 2*).

TABLE 2. COAGULATION OF SKIM WITH SURFACTANT AND CALCIUM CHLORIDE

Surfactant (%)	Calcium chloride (%)	Coagulation efficiency after 48 h
0.1	-	Incomplete
0.1	0.50	Incomplete
0.1	0.75	Almost complete
0.1	1.00	Complete
0.1	2.00	Complete

As the concentration of calcium chloride was increased the coagulation efficiency improved, with 1% calcium chloride giving complete coagulation in about 48 hours. Further increases in calcium chloride content made the coagulum harder; so 0.1% surfactant and 1% calcium chloride were used in future experiments.

Effect of Various Types of Calcium Chloride on Coagulation

Skim de-ammoniated to about 0.1% (pH 8.9) was treated in 1-gal quantities with analar, fused porous lump and commercial grade calcium chloride (all at 1% concentration). All three types of calcium chloride gave a similar degree of coagulation efficiency after three days. The experiment was repeated with the addition of 0.1% surfactant and similar results were again obtained.

Large-scale Production of Coagulum

Three tanks of de-ammoniated skim, each containing 5000 gal, were allowed to coagulate. The first tank was treated with 0.1% surfactant and 1% calcium chloride, the second with sulphuric acid to reduce the pH from 9 to 4, while the third was allowed to coagulate spontaneously. Coagula were processed after two days, one day and four days respectively, by which time complete coagulation had occurred. Because of the shorter coagulation time the coagulum treated with surfactant +

TABLE 3. TECHNOLOGICAL PROPERTIES OF SKIM RUBBER FROM THREE METHODS OF COAGULATION

Property	Sulphuric acid coagulation	Spontaneous coagulation	Surfactant + calcium chloride coagulation
Nitrogen (%)	1.97	1.69	1.57
Copper (p.p.m.)	6.00	10.90	1.20
Manganese (p.p.m.)	1.40	<1.00	2.30
Dirt (%)	0.04	0.05	0.01
Ash (%)	0.53	0.44	0.70
Volatile matter (%)	1.49	1.19	1.31
Acetone extract (%)	7.60	7.70	7.40
PRI	36.00	38.00	64.00
Mooney viscosity (ML 1 + 4 at 100°C)	78.50	83.00	80.00

TABLE 4. VULCANISATE PROPERTIES OF SKIM RUBBER FROM THREE METHODS OF COAGULATION (ACS 1 COMPOUND^a)

Property	Sulphuric acid coagulation	Spontaneous coagulation	Surfactant + calcium chloride coagulation
Cure at 140°C (min)	40	40	40
Tensile strength, kg/cm ² unaged	232	245	248
aged for three days at 100°C	96	120	115
retention (%)	41	49	46
Elongation at break, unaged (%)	580	670	670
aged for three days	380	440	470
retention (%)	66	66	70
Modulus 300%, kg/cm ² unaged	40	35	33
aged for three days	68	59	45
retention (%)	170	169	136
Relaxed modulus (kg/cm ²)	13.6	12.3	12.3
Hardness, IRHD	53.0	51.5	51.5
Dunlop resilience (%)	83	84.9	85.7
Mooney compound viscosity, (ML 1 + 4 at 100°C)	57.5	50	49.5
Mooney scorch time at 120°C (min)	2.0	4.4	4.3

^aParts by weight: rubber 100; zinc oxide 6; stearic acid 0.5; MBT 0.5; sulphur 3.5

salt was much less smelly than that which had coagulated spontaneously.

Technological Properties

The raw rubber properties of surfactant/calcium chloride rubber compare favourably with those of spontaneously-coagulated rubber, with a much lower copper content and high PRI value, but with a slightly higher ash content (*Table 3*). The nitrogen content of both rubbers is lower than that of acid-coagulated rubber.

Curing and vulcanisate properties of both surfactant/calcium chloride and spontaneously-

coagulated rubbers show advantages over the acid-coagulated rubber, having increased scorch time, lower relaxed modulus, tensile modulus and hardness, higher resilience and correspondingly lower heat build-up (*Tables 4 and 5*). There is little difference in ageing and other vulcanisate properties between the three rubbers.

DISCUSSION

The total production of latex concentrate in Malaysia was about 158 400 tonnes (dry rubber) in 1970 and the consequent skim rubber output about 12 700 tonnes. The

TABLE 5. VULCANISATE PROPERTIES OF SKIM RUBBER FROM THREE METHODS OF COAGULATION (TREAD COMPOUND*)

Property	Sulphuric acid coagulation	Spontaneous coagulation	Surfactant + calcium chloride coagulation
Tensile strength (kg/cm ²)	190	205	208
Elongation at break (%)	550	450	470
Modulus 300% (kg/cm ²)	136	138	130
Relaxed modulus (kg/cm ²)	27.7	26.8	25.8
Hardness, IRHD	76	75.5	75.5
Dunlop resilience (%)	52.6	53.9	54.7
De Mattia flex life, kc to grade C	85	100	110
Cut growth, kc to give crack growth			
2 - 4 mm	1.0	2.0	2.25
4 - 8 mm	15.25	9.5	10.75
8 - 12 mm	36.25	40.5	39.5
Tear strength (kg)	21.5	24	27.5
Goodrich heat build-up temperature after 60 min (°F)	274	246	258
Dynamic compression set (%)	44.10	29.5	37.0
Mooney compound viscosity, (ML 1 + 4 at 100°C)	74	67	70

*Parts by weight: rubber 100; zinc oxide (ICI Red Seal) 4.0; stearic acid 1.5; CBS 0.5; sulphur 2.5; HAF black (Acaib 45; Dutrex R 5.0; Nonox ZA 1.5

amount of skim rubber produced is so large that it is important to look at all possible methods of recovering this material. The traditional practice of recovery by acid coagulation results in a clean but very fast-curing and scorchy rubber because of the large and variable amounts of non-rubber constituents, particularly protein, which are present. Chemical deporteinisation of skim rubber improves the technological properties, but the chemicals involved are either caustic or expensive, making the process less practical and economical.

Spontaneous coagulation is not only economical but also results in good quality rubber. Its drawbacks, however, are that it takes about five days to complete, posing problems in the processing factory and producing foul-smelling coagulum and dry rubber.

When 0.1% surfactant and 1% calcium chloride are added to partially de-ammoniated latex a remarkable reduction in coagulation time is observed, a firm and less smelly coagulum being obtained in about two days. Surfactant (0.2%) and molasses (5%) also

accelerated coagulation and reduced the smell, but these levels of additives are not considered economical.

The surfactant + calcium chloride skim rubber compares favourably in its technological properties with spontaneously-coagulated rubber, both being superior to acid-coagulated skim rubber. This is to be expected as bacteria present in skim are capable of metabolising a variety of non-rubber constituents, resulting in end-products with acceptable properties (JOHN 1966b and c). Thus, the nitrogen content is reduced (presumably by protein degradation by proteolytic bacteria) leading to improved scorch time and resilience and reduced hardness, modulus and heat build-up. Surfactant/calcium chloride coagulated rubber has a satisfactory PRI value, while the other two coagulation systems produce rubbers with poor PRI.

It is also observed that poor PRI values are related to high copper contents. This observation is in agreement with the finding of BATEMAN AND SEKHAH (1966) that copper is a potent oxidant. The ash content of surfactant/calcium chloride rubber is slightly higher as part of the salt (calcium chloride) is likely to be left behind as a residue. On the other hand, it is possible that the presence of calcium chloride may have contributed to the improved scorch time (RESING, 1961).

The cost of surfactant + calcium chloride is approximately 0.25 ct (M) per pound of dry rubber. This is not considered unfavourable in view of the saving on the additional coagulation tank capacity required for spontaneous coagulation and the better quality rubber obtained.

ACKNOWLEDGEMENT

The authors are grateful to Mr Sripathi Rao, Head of Pathology Division, for help in the manuscript, to Encik Abdul Latiff bin Abdul Majid for laboratory assistance, to members of Chemistry Division for technological tests and to Guthrie Rubber Processing Sdn Berhad, Siliau, for the supply of skim latex

and assistance in applying accelerated biological coagulation to large-scale skim rubber production.

Rubber Research Institute of Malaya

Kuala Lumpur

March 1970

REFERENCES

- BAKER, H.C. (1958) Rubber from centrifuged skim latex. *Rubb. Dev.*, 11(1), 2.
- BARNWELL, T.H. (1957) Latex skim: the Dunlop process. *Plrs' Bull. Rubb. Res. Inst. Malaya No.33*, 108.
- BATEMAN, L. AND SEKHAH, B.C. (1966) Significance of PRI in raw and vulcanised natural rubber. *J. Rubb. Res. Inst. Malaya*, 19(3), 133.
- FIRESTONE TYRE AND RUBBER COMPANY (1955) Improvements in or relating to high grade rubber and method of making the same. *Br. Pat. No. 739 750*.
- JOHN, C.K. (1966a) Biological coagulation of Hevea latex using waste carbohydrate substrates. *J. Rubb. Res. Inst. Malaya*, 19(5), 286.
- JOHN, C.K. (1966b) Breakdown of amino acids by Hevea latex bacteria. *J. Rubb. Res. Inst. Malaya*, 19(4), 214.
- JOHN, C.K. (1966c) Metabolism of quebrachitol and other carbohydrates by Hevea latex bacteria. *J. Rubb. Res. Inst. Malaya*, 19(4), 219.
- JOHN, C.K. (1971) Coagulation of Hevea latex with surfactant and salt: I. Development of the process and its effect on raw rubber properties. *J. Rubb. Res. Inst. Malaya*, 23(2), 147.
- JOHN, C.K. AND PILLAI, N.M. (1971) Improvements to assisted biological coagulation of Hevea latex. *J. Rubb. Res. Inst. Malaya*, 23(2), 138.
- MORRIS, J.E. (1954) Improved rubbers by the enzymatic deproteinisation of skim latex. *Proc. 3rd Rubb. Technol. Conf. London 1954*, 13.
- RESING, W.L. (1961) Observations on the properties of skim rubbers. *Proc. nat. Rubb. Res. Conf. Kuala Lumpur 1960*, 686.
- SEKHAR, B.C., CHIN, P.S., GRAHAM, D.J., SETHU, S. AND O'CONNELL, J. (1965) Heveacrumbs. *Rubb. Dev.*, 18(3), 78.
- SMITH, M.G. (1969) Recent aspects of block natural rubber production by mechanical methods. *J. Rubb. Res. Inst. Malaya*, 22(1), 78.