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Assisted Biological Coagulation of Latex using Starch as a Supplementary Substrate

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An improvement to assisted biological coagulation (ABC) of natural rubber latex is effected by the addition of starch. A complete coagulation is achieved in 20 h, with pH of the serum being close to that of acid coagulation. The properties of the resulting rubber are comparable to those obtained from the ABC process.

The process of assisted biological coagulation (ABC) of latex has overcome some of the disadvantages of natural coagulation, such as length of time, incomplete coagulation and the development of malodour in the finished product (JOHN, 1966). The ABC process may therefore be useful in the production of block rubber. Recently, CHIN *et al.* (1972) have shown that PRI and mooney viscosity of the rubbers processed by this method are intermediate between those of acid-coagulated and autocoagulated rubbers. KRISHNASWAMY (1971) has shown that the initial pH of coagulation is important to maintain a consistent PRI value, particularly when there is delay in the processing of the coagulum; a high pH leads to a lower PRI.

This paper reports investigations in the laboratory and in a pilot plant on the use of starch as an additional substrate for the ABC process in an attempt to produce a rubber of improved PRI. It shows that by adding gelatinised starch to latex pretreated with molasses, a complete coagulation is achieved in about 20 h, the resulting rubber having comparable technological properties to those obtained from the ABC process using molasses alone.

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EXPERIMENTAL

Latex

For the laboratory investigations, fresh latex from PB 86, Tjir 1 and RRIM 513 clones was bulked, nearly in equal proportions. For pilot-plant trials, latices from a wider variety of clones were used, the more important of them being RRIM 500, 513, 623 and 600; PB 86, 5/63 and 5/51, Chemara 26 and Chemara 'E' garden. To prevent discolouration of the bulked latex, 0.04% sodium metabisulphite was added. All additions to latex, whether of chemicals or substrates, were made on the basis of the dry rubber content (d.r.c.).

Substrates

Sugar used in this experiment was the purified commercial form, containing more than 99.0% sucrose. Molasses containing about 50% total sugar was obtained from a nearby sugar refinery. Starch used was tapioca flour prepared as a gelatinised solution in water by heating at 70°C. Sugar and molasses were added as 5% and 10% solutions respectively and starch as 3% solution in water.

Bacterial Evaluation

The number of bacteria present in latex or serum was assessed by pour-plating 1 ml

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inocula from serial ten-fold dilutions using molasses/yeast extract agar (JOHN, 1968), incubating at 30°C for three days and counting by the method of JOHN AND TAYSUM (1963). The number of acid-producing bacteria in a sample was estimated by counting the acid-producing colonies (differentiated from the rest by the yellow hallow around them) in the most suitable dilution plate.

Pilot-plant Trial

Field latex bulked from various sources was treated with 0.04% metabisulphite and divided into three portions. To the first portion was added 0.4% molasses and to the second 0.4% molasses and 0.5% starch; the third portion received no treatment. All treatments were left to coagulate overnight, and on the following morning the coagula were processed as Dynat WL (SMITH, 1969).

Technological Testing

The rubbers obtained from the pilot-plant trials were tested for technological properties using an ACS 1 mix and a tyre tread compound. The composition of the ACS 1 mix was: rubber 100 parts, zinc oxide 6, stearic acid 0.5, MBT 0.5 and sulphur 3.5. The composition of the tread compound was: rubber 100 parts, stearic acid 2.0, Industry Reference Black (No. 2) 50.0, zinc oxide 4.0, Nonox ZA 1.5, Santoflex (13) 1.0, Dutres R 5.0, sulphur 2.5 and TBBS 0.5 parts.

RESULTS

Effect of Sugar or Starch on pH of Coagulation and Bacteria

The effect of sugar and/or starch on the pH of coagulation is shown in *Table 1.* Increase in sugar content did not reduce the pH of serum, but increase in starch content reduced it to 5.5 with 1.0% starch. In the combined presence of sugar and starch the drop in pH was even more marked, 0.2% sugar and 1.0% starch reducing it to 5.11, and 0.5% sugar and 1.0% starch to 5.06 in about 20 hours.

TABLE 1. EFFECT OF REFINED SUGAR AND/OR STARCH ON THE COAGULATION OF FIELD LATEX

Sugar (%)	Starch (%)	pH Initial (latex)	pH Overnight (serum)	Δ pH
Control	–	6.62	6.26	0.36
0.1	–	6.52	5.98	0.54
0.2	–	6.43	6.06	0.37
0.5	–	6.38	6.04	0.34
1.0	–	6.43	5.81	0.62
–	0.2	6.48	6.15	0.33
–	0.5	6.38	5.97	0.41
–	1.0	6.30	5.50	0.80
0.2	0.2	6.46	5.90	0.56
0.2	0.5	6.43	5.86	0.57
0.2	1.0	6.43	5.11	1.32
0.5	0.2	6.42	6.03	0.39
0.5	0.5	6.33	5.42	0.91
0.5	1.0	6.37	5.06	1.31

Bacterial population of the serum is related to its pH. The mean population in serum obtained from latex treated with sugar and/or starch is given in *Table 2.* A correlation was noticed between the viable population and the number of acid-producing colonies; when the viable population dropped from log 8.98 to 7.79 per ml, the number of the acid-producing colonies also dropped.

Effect of Molasses or Starch on Coagulation

The effect of molasses or starch, or their combination on the pH of coagulation, is given in *Table 3.* When the concentration of molasses was increased from 0.2% to 2.0% pH of the serum dropped from 6.08 to 5.39

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TABLE 2. EFFECT OF SUGAR AND STARCH ON BACTERIA OF SERUM

Treatment		Initial pH of latex	pH	Viable bacterial count (log/ml)	Number of acid-producing colonies on 10^{-7} plate
Sugar (%)	Starch (%)				
–	–	6.66	6.06	8.98	100
0.2	–	6.66	5.95	8.83	72
0.2	0.5	6.65	5.55	8.49	38
0.2	0.75	6.65	5.20	7.79	23

in about 20 hours. Likewise when the concentration of starch was increased from 0.2% to 1.0%, pH dropped from 5.81 to 4.78. The combined effect of molasses and starch was even better, 0.4% molasses and 1.0% starch reducing the pH to 4.49.

TABLE 3. EFFECT OF MOLASSES AND/OR STARCH ON COAGULATION OF FIELD LATEX

Molasses (%)	Starch (%)	pH Initial (latex)	pH Overnight (serum)	△ pH
Control	–	6.32	6.11	0.21
0.2	–	6.31	6.01	0.30
0.4	–	6.30	5.93	0.37
1.0	–	6.30	5.76	0.54
2.0	–	6.32	5.36	0.96
–	0.2	6.34	5.81	0.53
–	0.5	6.34	5.57	0.77
–	0.75	6.28	5.14	1.14
–	1.0	6.24	4.78	1.46
0.4	0.2	6.45	5.49	0.96
0.4	0.5	6.44	5.10	1.34
0.4	0.75	6.49	4.94	1.55
0.4	1.0	6.43	4.49	1.94

Effect of Coagulation System and Maturation on PRI

To find out the effect of coagulation system and maturation of the coagulum on PRI, bulked latex treated with sodium metabisulphite was divided into three lots. The first lot was treated with 0.4% molasses, the second with 0.4% molasses and 0.5% starch and the third lot was left without treatment. Coagula from the three systems were processed at various intervals, and the dry rubber tested for PRI *(Figure 1)*.

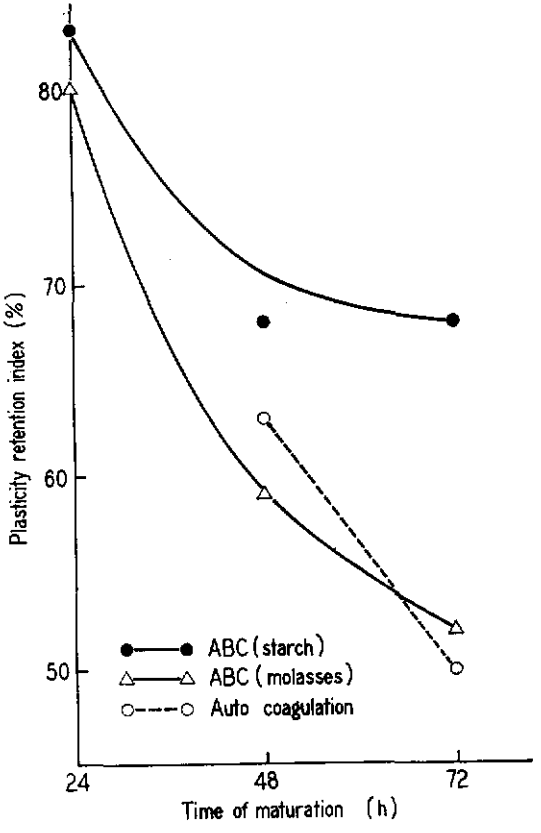

Figure 1. PRI of rubbers obtained from different coagulation systems.

The coagulation system containing molasses and starch gave higher PRI than the other two systems irrespective of maturation period. After 72 h of maturation, PRI of the former was about 68, while those of the latter two were around 50. Further, it was observed that maturation of coagulum lowered the PRI of the resulting rubber, irrespective of coagulation system, though this was less marked in starch-coagulated rubber.

In comparison to molasses alone being used, it was noted that starch used in the ABC system as a supplementary substrate gave a consistent and high level of PRI. The PRI results are given in *Table 4*.

TABLE 4. RESULTS OF Po AND PRI

Test reference	Property	Coagulation system ABC (molasses)	ABC (starch)
SSW/KHO/STD	Po	50.5	47.5
	PRI (%)	78	83
SSW/KHO/STD	Po	55.0	47.5
	PRI (%)	82	88
Trial No. 5 Chemara Research 24 h	Po	54.0	47.0
	PRI (%)	80	83
Trial No. 4 Chemara Research 24 h	Po	46.0	45.0
	PRI (%)	76	87
Trial No. 5 Chemara Researce 48 h	Po	41.0	44.0
	PRI (%)	59	68
Trail No. 5 Chemara Research 72 h	Po	44.0	47.0
	PRI (%)	52	68

Pilot-Plant Trials

Coagulation efficiency. The efficiency of various coagulation systems observed after about 20 h is given in *Table 5*.

While the addition of molasses to field latex substantially improved the coagulation efficiency, the combined addition of molasses and starch further enhanced it. While autocoagulation was incomplete, producing milky serum, treatment with molasses was nearly complete; but with molasses and starch complete coagulation was obtained, the resulting serum being very clear with a pH of 5.06.

Technological properties. Raw rubber properties of the rubbers prepared from coagula obtained from these three coagulation systems are given in *Table 6*. Comparatively higher values of ash, acetone extract, water extract and Mooney VR were observed in the system using molasses alone, while slightly higher nitrogen and PRI values were obtained when starch was incorporated in addition to rubber. The difference in cure rate was negligible.

All coagulation systems gave comparable vulcanisate properties *(Table 7)*.

The technological evaluation was repeated on a second series of samples prepared under identical conditions but using a different day's crop. On the raw rubber properties, the second series followed the same trend as the first. Cure rate difference was small. The vulcanisate properties in a tread mix showed ABC with starch to be comparable to ABC with molasses. No

TABLE 5. EFFECT OF MOLASSES AND STARCH ON COAGULATION

Treatment	pH of latex after substrate addition	Appearance of coagulation	Serum pH	Serum Clarity
No additions) Autocoagulation)	6.60	Incomplete	6.19	Very milky
Molasses (0.4%)	6.49	Nearly complete	5.75	Turbid
Molasses (0.4%) + Starch (0.50%)	6.46	Complete	5.06	Clear

TABLE 6. RAW RUBBER PROPERTIES

Property	Acid coagulation[a]	Molasses	Molasses + starch
Colour (Lovibond unit)	3.5	4.5	4.5
Ash (%)	0.17	0.28	0.26
Dirt (%)	0.008	0.008	0.009
Nitrogen (%)	0.42	0.42	0.46
Acetone extract (%)	3.21	2.82	2.68
Volatile matter (%)	0.28	0.31	0.30
Water extract (%)	0.42	0.66	0.48
Mooney VR, initial ML 1 + 4 at 100°C	88.3	91.3	83.3
Wallace plasticity, unaged (Po)	57.0	53	48
Aged (Pa)	48	42	41
PRI	84	80.0	85
MR 100 (MN m^{-2})	0.60	0.66	0.63

[a]This sample is from a different source of latex and is included only for easy reference.

TABLE 7. VULCANISATE PROPERTIES OF RUBBER (TREAD MIX)

Property	Acid coagulation[a]	Molasses	Molasses + starch
Mooney ML 1 + 4 at 100°C			
VB	79.5	78.0	84.0
VC	57.0	57.0	60.2
Scorch time (min)	18.0	16.5	16.8
Tensile strength (MN m^{-2})	27.6	27.1	27.7
Elongation at break (%)	575	553	565
Modulus 300% (MN m^{-2})	11.4	11.9	11.9
Hardness (IRHD)	62.0	62.7	63.1
Dunlop resilience (%)	58.5	57.9	58.5
Goodrich flexometer heat build-up			
Temp. (0°C) rise after 25 min	24.5	24.4	25.6
Temp. (0°C) rise after 60 min	48.4	43.9	48.1
Aged three days at 100°C			
Tensile strength (MN m^{-2})	20.5	20.8	20.6
Elongation at break (%)	373	353	368
Modulus 300% (MN m^{-2})	16.1	17.1	16.9

[a] This sample is from a different source of latex and is included only for easy reference.

significant difference in flex-cracking resistance was observed confirming the suspicion that the better values obtained for the ABC (molasses) in the first evaluation could be a result of slight differences in mixing conditions.

DISCUSSION

It is generally understood that bacteria prefer relatively simpler molecules of monosaccharides and di-saccharides to complex molecules of polysaccharides such as starch. The sharp drop in 20 h in the sole presence of starch, approaching the level that obtained with acid coagulation, was therefore unexpected. It is not clear from this study why starch is more readily metabolised than simpler sugars.

The relatively low pH values obtained when starch is used, might have been expected to enhance bacterial activity; yet, neither the total viable count nor the number of the acid-producing colonies showed a higher value. On the other hand, the coagulation system with higher pH gave higher bacterial counts and acid-producing colonies. The absence of any correlation between acid-production and the number of acid-producing bacterial colonies suggests that it is not the number of the acid-producing colonies that governs the acidity of the serum but their metabolic activities. Another point for consideration is that, since the bacterial counting of the serum has been made only after the pH had dropped to the low level, it cannot be regarded as a true indication of the nature of metabolic activity during the early stages of coagulation.

Starch alone markedly reduced the pH of coagulation to 5.57, but together with molasses further reduction to 5.51 was obtained. Further, the molasses/starch combination was even better than the sugar/starch combination in this respect. This is to be expected, as molasses contains up to 25% monosaccharides (which will be broken down in preference to di-saccharides) and other non-sugar materials.

A high PRI value for the dry rubber is a desirable property, PRI being a measure of the oxidisability of raw rubber (BATEMAN AND SEKHAR, 1966). KRISHNASWAMY (1971) has shown that a PRI value close to that of acid-coagulated rubber is possible from the biologically coagulated rubbers, by keeping the pH of coagulation at equivalent levels. The ABC system with starch, in addition to molasses, achieves this. With the pH of coagulation being around 5.0, PRI of the rubber resulting from a 20-h coagulation was found to be 86 units.

GRAHAM AND MORRIS (1966) have shown that maturation of coagulum has adverse effect on PRI; but according to KRISHNASWAMY (1971) a relatively high PRI can be achieved even if the coagulum is matured, provided the pH of coagulation is kept relatively low. The present work has shown that, irrespective of maturation period, the ABC process with molasses/starch gave higher PRI than auto-coagulation with or without molasses alone; after 72 h of maturation, PRI of the former was about 68 units compared to 50 units from the other two systems. The technological properties of the rubbers obtained from the ABC process with molasses/starch were satisfactory and were comparable to the properties of rubber obtained from ABC process using molasses alone.

The cost of the new coagulation system would vary depending on the availability and price of starch. At 25 Malaysian cents per kilo of starch, the process would entail an additional expenditure of about 0.25 Malaysian cents per kilo of dry rubber, but it is quite acceptable considering the advantages of the process.

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