Biological Coagulation of Hevea Latex Using Waste Carbohydrate Substrates

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Latex was coagulated in the presence of molasses and waste pineapple juice, with or without latex serum as a seeding inoculum. A near-complete coagulation—in the form of a spongy coagulum—was obtained in 16 hours with 0.2% (sugar on d.r.c.) of molasses or pineapple juice. The carbohydrate additives expedited the natural coagulation of latex by indigenous microbial population. The latex serum further speeded up coagulation but it also led to the production of malodorous rubber. The addition of pineapple juice gave a rubber golden yellow in colour and with pleasant odour while molasses-treated rubber was paler but had an equally agreeable odour. It was found that rubbers derived from biological coagulation in the presence of molasses and pineapple juice possessed faster curing characteristics. The technological properties of the resultant rubber were found to be satisfactory, provided the coagulum was processed with minimum delay. Development of the biological coagulation process is thus attractive because of the speed of coagulation, the low price and ready local availability of carbohydrate additives, the suitability of the coagulum produced to new presentation processes as well as the good physical appearance and pleasing odour of the product generally.

Sterile *Hevea* latex is stable (McMULLEN, 1951); but, when heavily contaminated with micro-organisms, it becomes unstable and coagulates rapidly (TAYSUM, 1958; JOHN and TAYSUM, 1963). Dry rubber is usually prepared from *Hevea* latex by coagulation with formic or other acids to reduce its pH (to 4.8–5.2 range). The acidified latex thickens and, after several hours, coagulates completely; a firm coagulum and a clear serum result. Latex may undergo spontaneous coagulation due to bacteria and yeasts which metabolise the non-rubber substances in it (ALTMAN, 1947; JOHN, 1966a and 1966b); coagulation is usually complete in about 48 hours. There are four disadvantages pertaining to the natural process: it is time-consuming, the coagulation is often incomplete, it produces varying degrees of offensive odour in the finished dry rubber and the ageing properties of the product are relatively unsatisfactory. An investigation was therefore carried out towards reducing or eliminating these drawbacks while retaining, at the same time, the advantages of natural coagulation. It was thought that many of the disadvantages in natural coagulation could also be overcome by speeding up the process. This was attempted by increasing the carbohydrates available for microbial breakdown to acidic derivatives (RUBBER RESEARCH INSTITUTE OF MALAYA, 1966).

EXPERIMENTAL

Molasses (containing approximately 50% sugar) and pineapple juice (8–10% sugar) were used as carbohydrate substrates. Both are readily available in Malaysia, and in considerable quantities. Seeding was also carried out with 24-hour-old latex serum which is rich in nutrients and which also contains a large number of micro-organisms (approximately 10^9 per ml).

Four levels of molasses (0.1, 0.2, 0.3 and 0.4% sugar on d.r.c.) and nine levels of pineapple juice (0.1, 0.15, 0.2, 0.3, 0.5, 0.75, 1.0, 1.5 and 2% sugar on d.r.c.) were used as additives. Undiluted latex was coagulated by stirring in the carbohydrate substrate, with or without latex serum, in 10-gallon tanks or one-

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TABLE 1. EFFICIENCY OF THE VARIOUS SYSTEMS OF BIOLOGICAL COAGULATION

Treatment	Initial pH	24-hour-old serum		Time of gelling, in hours	Finished product	
		pH	d.r.c. (%)†		Odour	Colour
Latex (natural coagulation)	6.61	6.02	3.98	14	Unpleasant	Pale yellow
Latex+acid	4.99	4.81	0.59	0.5	Pleasant	Light brown
Latex+latex serum, 50% on d.r.c.	6.35	5.51	2.32	6	Malodorous	Pale yellow
Latex+molasses, 0.2%	6.60	5.67	1.57	10	Sweet-smelling	Pale yellow
Latex+molasses, 0.2%+latex serum	*6.30*	*5.45*	*1.72*	*5.5*	*Unpleasant*	*Pale yellow*
Latex+pineapple juice, 0.2%	6.62	5.55	1.24	11	Sweet-smelling	Golden yellow
Latex+pineapple juice, 0.2% +latex serum	6.33	5.44	1.26	6	Unpleasant	Pale yellow

† The d.r.c. of the latex serum was estimated by mixing a certain quantity of it to a latex concentrate sample of known d.r.c.

gallon pans. Molasses was added as a 10% solution in water, but the coagulation itself was carried out omitting the usual flooding of the coagulum with water since enzymic discoloration does not usually occur with biological coagulation.

RESULTS AND DISCUSSION

A near-complete coagulation (>99.5%) was obtained with 0.2% (sugar on d.r.c.) of molasses or pineapple juice; higher levels of substrate somewhat reduced the coagulation time but did not influence the technological properties of the product. It was also observed that a moderate use of anticoagulants—upto 0.02% ammonia, 0.02% formaldehyde and 0.03% sodium sulphite—did not affect detectably the efficiency of biological coagulation. The coagulum was spongy, with many bubbles produced by microbial fermentation, in contrast to the bubble-free appearance of the relatively harder coagulum (pH: less than 5) from acid coagulation. The natural coagulum, processed after 16 hours, could be readily crumbled, minced or comminuted. The procedures regarding crumbling (SEKHAR AND CHIN, 1964; SEKHAR *et al.*, 1965), mincing (THOMPSON AND HOWORTH, 1964) and comminution (FLEUROT, 1965) have already been described. The coagulum was also processed *into sheets or crepe without difficulty.*

The crumbled rubber coagulated in the presence of waste pineapple juice was golden yellow in colour and pleasant in odour; that coagulated in the presence of molasses was paler, but equally pleasant in odour. Addition of latex serum to seed the latex reduced coagulation time to almost half, but did not contribute to a more complete coagulation. The addition of serum did not alter the colour of the rubber derived by treatment with molasses but marred the attractive light colour of rubber coagulated in the presence of pineapple juice. Further, seeding with latex serum led to the rubber becoming malodorous (*Table 1*).

The pleasant smell of the rubber coagulated by the addition of carbohydrate substrates to latex may well be due to the fermentative breakdown by certain of the saccharolytic micro-organisms present. On the other hand, the objectionable odour of rubbers coagulated in the presence of latex serum could result from a breakdown by proteolytic organisms of *the nitrogenous materials present in the serum* (WHITBY, 1966). Sheets prepared by biological coagulation invariably contained gas bubbles which, of course, did not influence the technological properties of the rubber. However, the number of bubbles was considerably reduced by maturing the wet sheets at room temperature for 24 hours.

Rubbers derived from biological coagulation followed by immediate processing were found to be in no way inferior to those obtained by coagulation with formic acid as regards their

TABLE 2. RAW RUBBER PROPERTIES OF RUBBERS OBTAINED FROM A 24-HOUR COAGULATION

Property	Acid coagulation	Natural coagulation	Biological coagulation	
			Molasses	Pineapple juice
Ash, %	0.24	0.20	0.25	0.23
Nitrogen, %	0.45	0.43	0.39	0.44
Copper, p.p.m.	<1.0	<1.0	<1.0	1.1
Iron, p.p.m.	13.9	10.9	12.2	14.2
Acetone extract, %	3.0	3.3	3.2	3.1
Mooney Viscosity				
Before mastication	70.2	75.3	74.0	77.8
After mastication*	66.8	71.8	70.1	72.1
PRI. Before mastication	91.0	85.0	87.0	77.0
After mastication*	86.0	73.0	80.0	73.0

* For 3 min at 150°C

technological properties (*Tables 2, 3* and *4*). The use of pineapple juice and molasses above 0.2% sugar level, and seeding with latex serum did not further improve any technological property. Since biological coagulation achieved without prior dilution of latex conserves a larger part of the naturally occurring cure-accelerating substances, the rubber obtained is uniformly consistent and attractive in cure characteristics.

Biological coagulation lowers the cost of production, through savings in the use of anticoagulants, even more so of acids. As regards comminution or pelletisation, coagulum obtained from biological coagulation is processed and dried more easily because of its blown nature. Biological coagulation also reduces coagulation time from 48 to 16 hours in comparison with auto-coagulation.

The low price and ready availability of molasses and waste pineapple juice, the reduction in coagulation time, the suitability of the coagulum for communition, crumbling, mincing or sheeting and the good physical appearance of the finished rubber make the biological coagulative process attractive. Further work on the technological characteristics of these rubbers and the influence of processing factors is in hand.

TABLE 3. TECHNOLOGICAL PROPERTIES OF BIOLOGICALLY COAGULATED RUBBERS USING ACS. 1 MIX*

Property	Acid		Molasses	
	30†	40†	30†	40†
Tensile strength, lb/in²	2461	3016	2888	3114
Elongation at break, %	842	887	831	855
300% modulus, lb/in²	213	213	242	242
600% modulus, ,,	925	896	1138	1095
Hardness, BS°	39.3	39.1	40.6	40.9
Rebound resilience, %	82.2	83.2	83.0	82.4
TC strain, %		69		59

* ACS. 1 Mix: Rubber 100; Zinc oxide 6; Stearic acid 0.5; MBT 0.5; Sulphur 3.5

† Cure at 141°C, min.

TABLE 4. TECHNOLOGICAL PROPERTIES OF BIOLOGICALLY COAGULATED RUBBERS USING A TYRE TREAD COMPOUND*

Properties	Acid coagulation (24 hrs)	Natural coagulation (24 hrs)	Biological coagulation (24 hrs)	
			Molasses	Pineapple juice
Cure time 40 min. at 141°C				
Tensile strength, lb/in²	3790	3867	3812	3771
Elongation at break, %	519	529	510	511
300% modulus, lb/in²	1853	1854	1900	1874
Hardness, BS°	65.2	64.9	65.0	65.9
Rebound resilience, %	64.5	64.7	65.6	65.0
De Mattia flex life, kc to grade C	123	130	118	118
„ „ crack growth, kc to given crack growth				
2–4 mm	5.5	10.5	5.3	8.5
4–8 mm	69.5	80.5	76.8	67.0
8–12 mm	54.8	38.0	44.5	64.5
Tear strength, lb/in²	50.8	66.4	69.0	63.1
Heat build up—temperature (°F)				
25 min.	236	236	237	238
60 min.	245	247	246	246
Scorch time, min.	10.2	9.9	9.8	9.6
After 36 days ageing at 70° C				
Tensile strength, % retained	60.7	61.9	57.8	58.3
Elongation, „	69.3	61.4	60.6	60.7
300% modulus, „	120.9	122.2	114.5	115.2
Hardness, „	105.8	102.5	103.5	103.3
Resilience, „	88.7	92.0	89.3	90.6

* Mix: Rubber, 100; HAF (Philblack) black, 45; Pine tar, 5; Zinc oxide, 5; Stearic acid, 2; PBN, 1.0; CBS, 0.6; Sulphur, 2.5.

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