

ENZYME DEPROTEINIZATION OF HEVEA LATEX II THE USE OF PAPAIN IN RSS MANUFACTURE

P. A. J. YAPA AND W. A. LIONEL

SUMMARY

The use of papain treatment in RSS manufacture was investigated. The problem of prolonged drying time associated with enzyme coagulation was alleviated by using acid as part coagulant. Milling into a thinner sheet also reduced drying time. Papain treated sheets were found to be resistant to mould growth. Both papain treated rubber and papain/acid treated rubber were found to be suitable for cyclization with p-toluene sulphonic acid, using auto- and heat-initiation of the cyclization reaction, respectively. Raw rubber and technological properties of papain-treated sheets were satisfactory. Technological properties were adversely affected by the use of raw papaw milk.

INTRODUCTION

Deproteinization of NR is now well known to improve its technological and dynamic properties. Low heat build-up of low protein rubber enhances its suitability for important industrial applications, particularly tyre manufacture. Ribbed smoked sheet (RSS) is the grade of NR produced most commonly, especially by smallholders. It constitutes a major proportion of the total rubber production of many of the NR producing countries including Sri Lanka, where it represents as much as 58% of the total annual production. However, apart from the recent organization of Group Processing Centres for smallholders, quality improvement aspects of sheet rubber, have received very little attention, particularly in relation to improvements such as deproteinization.

The use of papain (dried papaw milk) as a coagulant in the manufacture of sheet rubber has been reported earlier by Nadarajah *et al* (1973). One of the advantages of this treatment is the resistance shown by the resulting rubber to mould growth (Yapa, 1975). However, problems such as longer drying time, slight discoloration and high ash content, when papain is used for coagulation, remain to be solved (Nadarajah *et al* 1973). The present study was undertaken to try to solve these problems whilst retaining the improved characteristics of papain-treated rubber. The use of raw papaw milk was also investigated.

MATERIALS AND METHODS

All experiments reported here were carried out at the Group Processing Centre at Kalupahana. White papain purchased locally was used in all trials. In studies with raw papaw milk (RPM), fresh RPM was collected from green papaw fruits; occasionally the RPM was preserved with sodium metabisulphite. RPM was added to latex as a suspension in water at a concentration of 0.05% papain of latex.

In the study on mould growth on sheets, the sample pieces of equal size (4" x 2.5") were placed vertically in a desiccator using an aluminium holder; a filter paper moistened with water was left at the bottom of the desiccator. The samples were taken out after two weeks and mould

was removed with water. The washings of each sample were combined and centrifuged to isolate the mould. The extent of mould growth was determined by weighing the mould after drying in a desiccator.

RESULTS

Drying time

Preliminary studies were carried out to confirm the findings of Nadarajah *et al* (1973) with reference to longer drying time and loss of dry weight when papain alone was used as a coagulant. Drying time of rubber from enzyme treated latex was always found to be high, irrespective of the final grade, unless the coagulum was milled into thin laces. Drying time was unacceptably high in the case of sheets when enzyme treatment was used as the method of coagulation. Although it was found that drying time of enzyme treated rubber can be considerably reduced by using the enzyme as a part coagulant with acid, it was still rather high. Therefore, an attempt was made to study the effect of reducing the thickness of sheets on drying time and the results are given in Table 1. Sheet samples were kept in an oven 60°C and the reduction in weight was recorded at 12 h intervals. It is seen that the use of acid as a part coagulant has a marked effect on reducing the drying time and this is further improved by reducing the normal thickness of the sheets. However the drying time of acid/papain coagulated rubber with reduced sheet thickness is still higher than that of acid coagulated sheets of normal thickness (Table 1).

TABLE 1. Effect of sheet thickness on drying time at 60°C

<i>Treatment/Thickness</i>		<i>Drying Time (hours)</i>
1. Acid/thick (2.20 mm)	...	63
2. Acid/thin (1.70 mm)	...	39
3. Acid/papain/thick (2.02 mm)	...	111
4. Acid/papain/thin (1.60 mm)	...	99
5. Papain/thick (2.60 mm)	171
6. Papain/thin (1.52 mm)	...	135

Mould growth

The nitrogen content of acid-papain coagulated rubber is intermediate between those of acid and papain coagulated rubbers as seen in Table 2. The effect of deproteinization on mould growth is shown in Table 3. The low nitrogen content of acid-papain coagulated rubber appears to exert an appreciable inhibition on mould growth on sheets. It is seen that the inhibitory action increases with the increasing concentrations of papain. The use of papain as a part coagulant with acid gives an inhibition of 44% on mould growth under the highly humid conditions employed in this experiment. The highest inhibition was observed when papain was used as the sole coagulant.

TABLE 2. Raw rubber properties of papain treated rubbers

<i>Property</i>	<i>acid/control</i>	<i>papain</i>	<i>papain & acid</i>	<i>RPM</i>	<i>RPM & acid</i>
N% wt	.35	.13	.21	.14	.22
Ash% wt	.20	.17	.19	.18	.19
Volatile matter % wt	.35	.70	.56	.45	.54
Dirt % wt	.02	.20	.30	.30	.03
Po	55	61	60	63	71
PRI	89.1	80.3	80.0	79.4	76.1
Mooney V.	69	74	73	79	80

TABLE 3. Effect of deproteinization on mould growth

<i>Treatment</i>	<i>Mould mg/cm²</i>	<i>% Inhibition</i>
1. acid only	0.45	—
2. acid $\frac{3}{4}$ + papain $\frac{1}{4}$	0.34	24.4
3. acid $\frac{1}{2}$ + papain $\frac{1}{2}$	0.25	44.4
4. acid $\frac{1}{4}$ + papain $\frac{3}{4}$	0.21	53.3
5. papain only	0.11	75.5

Mould growth on sheets was also investigated under normal storage conditions. Heavy mould growth was observed on normal sheets when both normal and papain treated sheets were stored in a poorly ventilated room for about 3 weeks. The inhibition of fungal growth on papain coagulated rubber in this trial was very marked and no mould growth was found even when the spores of the fungus were placed on to the sheets.

Raw rubber properties

The oxidation resistance, as indicated by the PRI of papain treated sheets, was found to be satisfactory. A slight reduction in the PRI was observed when raw papaw milk was used. Wallace plasticity (Po) was generally high in all papain treated sheets (Table 2.) The use of 100% papain had a slight adverse effect on the colour of the rubber, as the sheets were darker when compared with acid coagulated sheets. The combined treatment of papain and acid improved the colour, which was intermediate between acid and papain coagulated rubbers.

Raw papaw milk

Raw papaw milk (RPM) was tried out as a coagulant with or without acid. The various combinations of RPM and acid used are given in Table 4. Although it was found that RPM can be used as a coagulant, the loss of dry weight was unacceptably high, particularly when RPM was the sole coagulant; there being a 13.8% reduction compared with the acid control (Table 4). However, as far as the deproteinization is concerned, the use of RPM alone is very effective. The increase in Plasticity is even more marked in the RPM treatment compared to dried papaw milk (Table 4). RPM was also found to have an adverse effect on PRI (Table 4).

TABLE 4. Use of preserved papaw milk and loss of weight

<i>Treatment</i>		<i>Property</i>	
<i>2% HCOOH</i>	<i>Papaw milk</i>	<i>% loss of wt.</i>	<i>N%</i>
1. 180 cc:	—	—	0.58
2. 150 cc:	10 cc	0.09	0.53
3. 120 cc:	20 cc	0.2	0.46
4. 90 cc:	30 cc	1.8	0.29
5. 60 cc:	40 cc	6.5	0.21
6. 30 cc:	50 cc	8.6	0.18
7. —	60 cc	13.8	0.18

TABLE 5. Physical & Technological properties*

<i>Property</i>	<i>Acid</i>	<i>Acid/papain</i>	<i>Papain</i>
Hardness (IRHD Units)	44	38	36
Tensile strength (kg/cm ²)	89.2	79.5	78.4
Modulus at 300% (kg/cm ²)	15.4	14.1	13.3
Modulus at 500% (kg/cm ²)	32.3	26.5	21.2
Elongation at break %	700	750	722
Cure time (min)	68	70	68
Scorch time (min)	6	8.5	8

*ACS—1 Mix.

Technological properties

The physical and technological properties of ACS 1 Mix and filled compound are given in Tables 5 & 6, respectively. Papain treatment was found to affect the tensile strength in the ACS 1 Mix (Table 5). However, a significant improvement in tensile strength was found in the filled compound of papain treated rubber (Table 6). RPM treatment on the other hand, was found to have an adverse effect on tensile strength even in filled compound (Table 6).

TABLE 6. Technological & Physical properties* of enzyme treated rubbers

Property	Treatment				
	Acid/control	Papain	Papain + acid	RPM	RPM + acid
Scorch time/min	3	5	5	3½	3½
Cure/min	22½	19	21½	23½	23½
Cure Rate Index	5.12	7.14	6.15	5.12	5.00
Tensile Strength kg/cm ²	231.0	268.8	235.5	208.6	218.7
Modulus at 100% kg/cm ²	20.17	16.43	15.36	17.21	16.27
Modulus at 300% kg/cm ²	97.09	91.0	78.12	92.71	83.33
Elongation at break %	600	600	550	500	550
Hardness / IRHD	67	65	64	65	60
Resilience resistance %	60	62	61	59	61

*filled compound

DISCUSSION

The results reported in this paper indicate that papain can be advantageously used as a coagulant in RSS manufacture; resistance to mould growth and improvement of some technological properties are the main advantages of the enzyme treatment. Prolonged drying time of papain treated sheets appears to be the only disadvantage which needs further study. Although the present study shows that drying time can be reduced by using papain as a part coagulant with acid and also by reducing the thickness of sheets to half the normal thickness, it still remains rather high. The drying of enzyme treated rubbers has always been a problem (Nadarajah *et al*, 1973; Yapa, 1976; John & Nadarajah 1978), and is apparently associated with the retention of the hydrophilic nature of the remaining proteins; this is enhanced by the increased thickness of sheet rubber. The authors have also observed this behaviour in block rubber manufacture, when enzyme treatments were employed. Our experience is that the drying problem can be alleviated considerably by milling the coagulum into thin laces although it is impracticable in RSS manufacture. However, when sheets are milled into a thinner form than usual it affects the normal appearance of sheets; this in turn may be a disadvantage with the existing system of grading. In the context of improved technological properties, the application of the present grading procedure to low protein sheet rubber appears to warrant reconsideration. In addition to technological properties reported in this paper, the dynamic properties such as heat build-up have also shown an improvement in preliminary tests. This would enhance its suitability for tyre manufacture. In this context the separation of low protein rubber from the present grading system of sheet rubber based on purely visual assessment requires serious consideration.

One of the present major uses of papain treated rubber is in cyclised rubber manufacture. Thin laces (papain treated) which would otherwise have been used for crepe rubber manufacture, are utilized for cyclization. With the present demand and prices, the use of crepe rubber in cyclized rubber manufacture would lead to a considerable loss to the country in terms of foreign exchange earnings. The use of papain treated sheet rubber may be a suitable alternative, as sheet rubber is normally cheaper than crepe rubber. Cyclization of papain treated sheet rubber with *p*-toluene sulphonic acid has been found to be as good as that of papain coagulated thin laces. Acid-papain treated sheet rubber has also been found suitable with heat initiation (Yapa, 1979) for cyclization. Possible use of papain treated sheets in the cyclized rubber manufacture underlines the importance of classifying it as a special purpose rubber, thus eliminating the need for subjecting it to the conventional grading system based on external appearance.

The possibility of using raw papaw milk in sheet manufacture is not promising owing to several drawbacks such as the loss of dry weight (which was found to be as high as 13.8%), and adverse effects on the PRI and tensile strength. Loss of dry weight is presumably due to the preservative (sodium bisulphite) used resulting in an incomplete coagulation of latex. This can be overcome by using un-preserved fresh RPM. Although the PRI is not so severely affected, the effect of RPM on tensile strength is so adverse that it seems to rule out any possibility of using it in its present form. Further investigation is necessary in order to identify some of the adverse effects of RPM on technological properties.

ACKNOWLEDGEMENTS

We wish to thank Dr. O. S. Peries, Director and Mr. D. M. Fernando, Assistant Director, Rubber Research Institute of Sri Lanka for their valuable comments. Thanks are also due to Mr. M. D. C. Seneviratne for technical assistance.

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