Sri Lanka Journal of Food and Agriculture 3(1): 9-18, 2017
DOI: http://doi.org/10.4038/sljfa.v3i1.38

Sri Lanka Journal of Food and Agriculture (SLJFA)

ISSN: 2424-6913
Journal homepage: www.slcarp.lk

Research Paper

Raw rubber properties and mechanical properties of smoked sheet rubber made from natural rubber latex preserved using ammonia

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Article History:
Received: 26 January 2017
Revised form received: 28 June 2017
Accepted: 30 June 2017

Abstract: A study was carried out to understand the processing behaviour of smoked sheet rubber manufactured using natural rubber field latex (NRFL) preserved using ammonia at different concentrations. The NRFL preserved with sodium sulphite was used as a control together with un-preserved NRFL. The NRFL preserved using different ammonia concentrations were kept for different time intervals before further processing. Sheet rubber was manufactured using the preserved latex according to the standard manufacturing procedures. Preservation ability, acid requirement for coagulation, drying characteristics, and the raw rubber properties and mechanical properties of sheet rubber were evaluated. The results revealed that the ammonia concentration should exceed 0.15% to keep the latex for more than a day without pre-coagulation. As the ammonia concentration is higher, the acid requirement was higher. Sheet rubber manufactured using ammoniated latex takes marginally longer time to reach complete dryness. The ammonia concentration and time of preservation has a significant effect on raw rubber properties other than un-aged rapid plasticity number. There was no significant effect ($p>0.05$) on the mechanical properties other than aged-tensile, tear properties and rebound resilience at aged state.

Keywords: *Ammonia, natural rubber latex, drying characteristic, ribbed smoked sheet rubber, raw rubber properties*

Introduction

Natural rubber field latex (NRFL) exuded from the rubber tree (*Havea brasiliensis* Müll. Arg.) is a stable colloidal dispersion of natural rubber (cis 1.4 polyisoprene) agglomerates surrounded by a protective layer of proteins and phospholipids in an aqueous medium. It contains many other non-rubber constitutes such as protein, carbohydrates, antioxidants, fatty acids, enzymes and carotenoid like pigments, etc. As soon as exuded from the tree and exposed to the environment, latex has a tendency for pre-coagulation and putrification due to the bacterial action on non-rubbers present in the latex such as protein and carbohydrates. Consequently, formic, acetic and propionic acids are generated in latex. These acids neutralize the negative charges distributed around the rubber agglomerates causing unintended coagulation or pre-coagulation. Therefore, fresh NRFL has to be preserved with a suitable preservation system before it converts into industrially-valuable semi raw materials such as sheet rubber, crepe rubber, technically specified Standard Lanka Rubber (SLR) and centrifuge latex.

Sodium sulphite (Na_2SO_3), and ammonia are used as preservatives for latex depending on the type of raw rubber to be manufactured and intended duration of preservation. Sodium sulphite is the only preservative recommended to preserve the latex intended to be used for crepe rubber manufacture. In sheet rubber manufacture, both sodium sulphite and ammonia can be used as latex preservatives.

In Sri Lanka, the smallholder sector that dominates the manufacture of sheet rubber uses sodium sulphite as it is effective as a short-term preservative, which offers a good colour to sheet rubber. Therefore, at present, ammonia is rarely used as a preservative in sheet rubber manufacture as it tends to develop dark colour complex compounds on sheet rubber due to the reaction between ammonia and non-rubber substances present in the NRFL. However, it is the only effective primary preservative used for NRFL to control the development of volatile fatty acids (VFA) to keep the latex without being pre-coagulated for a few days, thus leaving sufficient time for collection and transportation for further processing, concentration, and coagulation.

When the field latex is inadequately preserved, VFA of latex would increase rapidly disqualifying the use of such latex for manufacturing centrifuge latex. This latex is then converted into sheet rubber as the next option. In addition, large scale latex collectors are also compelled to convert the latex into rubber sheets instead of processing them into latex concentrates to fetch the advantage of higher prices of sheet rubber in the favourable market scenarios. Being a chemically active constitute, rubber latex could react with non-rubber substance present such as lipids and proteins, forming complex compounds, salts and soluble products in the latex. Therefore, preservation with ammonia could affect the processing characteristic of sheet rubber, raw rubber properties and mechanical properties of the product. In literature, there is scarcity information on the effect of ammoniated latex on the above properties of sheet rubber made out of ammonia-preserved latex. Therefore, this study was carried out to understand the processing of ammoniated-latex into ribbed smoked sheet (RSS) rubber, their raw rubber properties and mechanical properties in comparison to that of the sheet rubber made out of latex preserved with sodium sulphite.

Materials and Methods

Field latex was obtained from the Dartonfield rubber estate that belongs to Rubber Research Institute of Sri Lanka, and preserved using different ammonia concentrations (0.05%, 0.1%, 0.15% and 0.2% ammonia on latex). Latex was preserved in separate containers for different periods (0 h, 24 h, 48 h,). A latex sample preserved using 0.05% sodium sulphite and preservative-free sample were used as the controls. Preservation systems used in study are shown in Table 1.

Table 1. Preservation systems and identification codes of latex samples

PP*[1] (h)	**Preservative and its concentration on latex**					
	Control	**Na_2SO_3 (0.05%)**	**NH_3 (0.05%)**	**NH_3 (0.10%)**	**NH_3 (0.15%)**	**NH_3 (0.20%)**
0	C-0	Na5-0	A5-0	A10-0	A15-0	A20-0
24	-	-	A5-24	A10-24	A15-24	A20-24
48	-	-	A5-48	A10-48	A15-48	A20-48

[1] Preservation period

The RSS were produced after standardization of latex by adding clean water to bring the dry rubber content (DRC) to 12.5%, as estimated according to the Metrolac reading (ZEAL 90/80165, 840 F, England). The samples were produced according to the standard method of RSS manufacturing. Latex was coagulated by adding 1% formic acid to bring the pH into the isoelectric point (4.4-4.8 pH) by using bromo cresol green (BCG) indicator prepared by dissolution of BCG powder [Hemsons (Pvt) Ltd., Sri Lanka]. In order to study the keeping time of ammonia in latex on the drying rate of sheet rubber, four sets of sheet rubber were prepared using latex withdrawn at different time intervals after addition of ammonia (0, 1, 2, 3, 5 h). For this purpose, latex preserved with 0.2% ammonia was used. Following properties were studied.

Processing characteristics

The processing characteristics measured were the (a) ammonia concentration of latex against the preservation time, (b) acid requirement to coagulate preserved latex and total alkalinity change with the time of preservation according to the standard method of IS: 3078 (Part 4) – 1985, and (c) the drying curve of the ammonia preserved samples were developed taking the rate of weight loss of sheets using oven drying method. Table 2 shows the sample used to study the drying characteristics.

Table 2. Identification codes of samples used for drying studies

PS*[1]	**Control**	**Na_2SO_3**	**NH_3**			
KT*[2] (h)	0	0	0	1	3	5
Code	C-0	Na5-0	A20-0-0	A20-0-1	A20-0-3	A20-0-5

[1]Preservation system, [2]Keeping time of preserved latex before coagulation (h)

Raw rubber properties

Selected raw rubber properties were evaluated according to international standard methods after manufacturing of RSS, namely, (a) Volatile Matter Content according to ISO 248: 1991(E), (b) Moony viscosity - ISO 289-1:1994(E), and (c) Plasticity Retention Index - ISO 2007:1991(E) and ISO 2930:1995(E)

Mechanical Properties

In order to study the effect of the preservation system on mechanical properties of rubber vulcanizate, sheets manufactured using latex preserved using 0.05% sodium sulphite (Na5-0) and 0.2% ammonia (A20-24) were compounded according to tyre trade compounding formula (Table 3).

Table 3. Tyre trade compounding formula (Chandrasekaran, 2007)

Chemical	**Amount (g)**
Natural Rubber	100.0
Carbon Black (N 330)	50.0
Processing oil	5.0
Zinc Oxide	4.0
Stearic acid	2.0
IPPD*[1]	1
PVI*[2]	0.15
CBS*[3]	0.8
Sulphur	2.2

[1]N-isopropyl-N′-phenyl-p-phenylenediamine, [2]N-(Cyclohexylthio)pthalimide; [3]N-cyclohexyl-2-benzothiazole sulphenamide

The compounded rubber samples were vulcanized for their respective cure times and mechanical properties such as the tensile properties - ISO 37: 1994(E), tear - ISO 34-1: 1994(E), abrasion resistance - DIN 53516 (1987), hardness - ISO 48: 1994(E), and rebound resilience - ISO 48: 1994(E) were measured.

Experimental design and data analysis

The total alkalinity, drying curve and the raw rubber properties were analysed with treatments being arranged in a randomized complete block design (RCBD) with three replicates. The mechanical properties were analysed with treatments being arranged in a complete randomize design (CRD) with three replicate. The results were analysis using MINITAB 16 at $p=0.05$.

Results and Discussion

Processing characteristics

Preservation time

Preservation time of field latex preserved with different ammonia concentrations are shown in Table 4. Field latex preserved with 0.05% sodium sulphite on latex (control sample) and with ammonia at 0.05% and 0.1% concentration on latex was auto coagulated after about 5, 8 and 24 h, respectively. At these concentrations of ammonia (0.05%, 0.1%), the mortality rate of bacteria is equal to its multiplication rate (Blackly, 1997). As per visual observation, latex preserved with ammonia at 0.15% and 0.2% on latex could be kept for more than 24 h and 48 h, respectively, without pre-coagulation.

Table 4. Preservation time of latex with different treatments

Preservative Concentration on latex	Minimum time taken to appear signs of pre-coagulation (h)
No preservative - Control	5
Sodium sulphite - 0.05%	8
Ammonia - 0.05%	24
Ammonia - 0.10%	24
Ammonia - 0.15%	24
Ammonia - 0.20%	48

Acid requirement and total alkalinity

The acid requirement for coagulation of latex preserved with different preservation systems after keeping for various time intervals are presented in Table 5. The control samples and the latex preserved at 0.05% Na_2SO_3 required similar quantity of acids for complete coagulation of latex in the same day of latex collection. However, when ammonia used as a preservative even at 0.05% concentration, a relatively high amount of acid was required. As the ammonia concentration is higher, the acid requirement and possible keeping time of latex without onset of pre-coagulation also increases. The consumption of acid was reduced with the keeping time of preserved latex. This was confirmed by the decrease in total alkalinity of the ammonia-treated latex samples with the keeping time of preserved latex. This could probably be due to the volatility of ammonia. The increase on ammonia concentration had a significant effect on the latex ($p<0.05$) and the time of preservation ($p<0.05$). The results suggested that time taken for latex collection and transportation could be extended by increasing the concentration of ammonia, but at the expenses of subsequent excess acid requirement for coagulation.

Drying curves for RSS produced from latex preserved with ammonia

Drying curves of the RSS produced from samples preserved in ammonia are illustrated in Figure 1. The weight loss of sheet rubber produced from ammonia-treaded samples were higher than that of the control ($p<0.05$), except in the sheet rubber produced from coagulation of latex just after the addition of ammonia. A significant effect on the weight loss of the samples was also observed with the increase in preservation time ($p<0.05$). This may be due to that the ammonia added to latex has gradually converted to ammonium salts with the hydrolysis of proteins and lipids. When formic acid is added as a coagulant, another salt of ammonia is also formed. All these salts have hygroscopic effect. As the preservation time is higher, the amount of ammonium salts formed in the latex will be higher and available in various forms. Lack of adequate time to form ammonia salts in latex may result in lower weight lost compared to other sheet rubber types made out of NRL preserved for a shorter period. Sheet rubber produced from latex preserved with 0.05% Na_2SO_3 on latex, also showed a higher weight loss than that produced from latex coagulated just after and one hour after addition of ammonia. This may be due to the formation of sodium salts, which also have hygroscopic characteristics.

Table 5. Acid consumption for complete coagulation and alkalinity at the time of addition coagulant

Sample*	1% formic acid (ml)	Alkalinity (w/w)
C-0	200	-
Na5-0	200	-
A5-0	300	0.019
A10-0	400	0.111
A15-0	900	0.121
A15-24	600	0.104
A20-0	1000	0.178
A20-24	900	0.177
A20-48	700	0.123

* C = Control, Na5 = Na_2SO_3 (0.05%), A5 = NH_3 (0.05%), A10 = NH_3 (0.10%), A15 = NH_3 (0.15%), A20 = NH_3 (0.20%); 0, 24 and 48 = time of addition of coagulants (h)

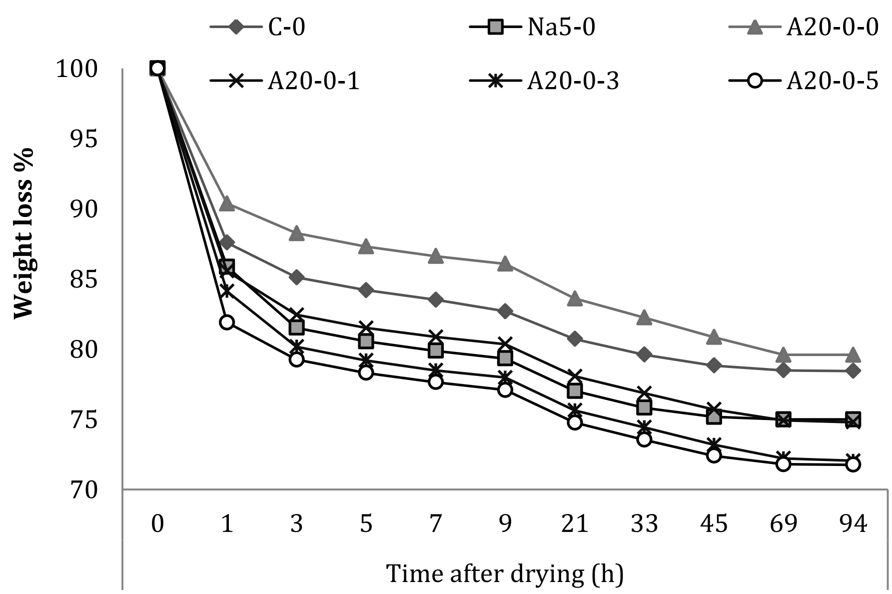

Figure 1. Drying curves of different sheet rubber types (see Table 2 for details on the codes given in the legend)

When assessed visually, following the industrial practice, the sheet rubber made out of latex unpreserved, preserved with Na_2SO_3, and just after ammonia-treatment achieved complete dryness earlier than that of other ammonia-treated latex samples. This may be due to the presence of high amount of hygroscopic materials in the latex samples as explained above.

Raw Rubber Properties

Volatile Matter Content

The volatile matter content (VMC) of RSS produced from latex treated with different concentrations of ammonia in comparison to the control sample and sheets produced from latex treated with Na_2SO_3 are illustrated in Figure 2.

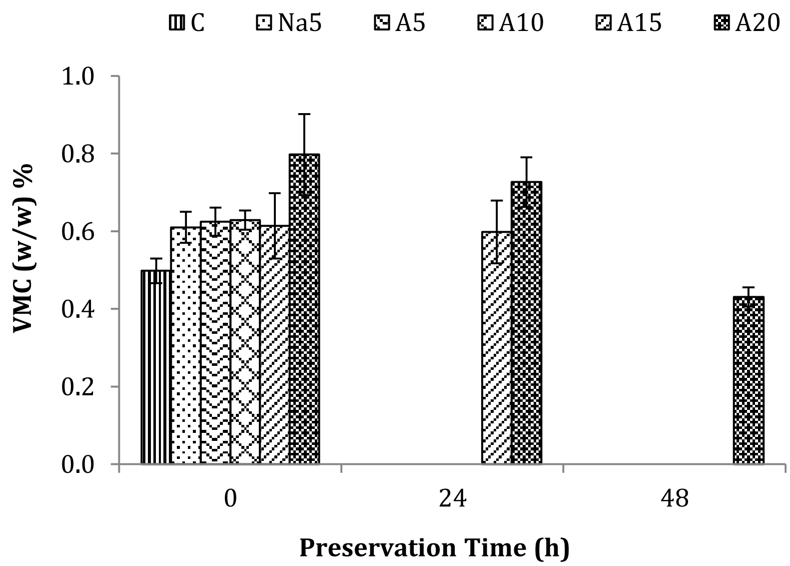

Figure 2. Comparison of volatile matter content (VMC) of the different rubber types. Vertical lines indicate the standard error of the means. C = Control, Na5 = Na_2SO_3 (0.05%), A5 = NH_3 (0.05%), A10 = NH_3 (0.10%), A15 = NH_3 (0.15%), A20 = NH_3 (0.20%)

Increase in the ammonia concentration has resulted in an increase in VMC (w/w) of the samples. This may be due to the presence of higher amount of ammonia salts on the surface of sheets as stated previously. The RSS produced from latex preserved with Na_2SO_3 (0.05% on latex sample) also showed a higher VMC compared to the control probably due to the hygroscopic nature of the sodium salts. There was a significant effect ($p<0.05$) of different preservation systems on VMC. Increase in time of preservation has decreased the VMC.

This result together with those of the alkalinity test (Table 5), which showed that the increase in time of preservation would lead to a decrease in the alkalinity of the samples, suggest the presence of lower amount of ammonium salts in those sheets. The results also indicated that the different times of preservation had a significant effect ($p<0.05$) on the VMC of the samples.

Moony viscosity

Changes in the Moony viscosity of RSS produced from different latex samples are illustrated in Figure 3. There was a significant effect of the different concentrations and times of preservation on the Moony Viscosity of the sample ($p<0.05$). It was evident that the ammonia-treated samples had a marginal increase in the Moony viscosity of sheets produced even after 24 h preservation, when compared to the control. Waddel (2005) reported that ammonia has the ability to increase the Moony viscosity even at a concentration 0.01% on latex, due to the formation of gel structure. Subramanium (2002) observed formation of various salts as a result of hydrolysis of proteins and phospholipids present in latex, which may increase the Moony viscosity.

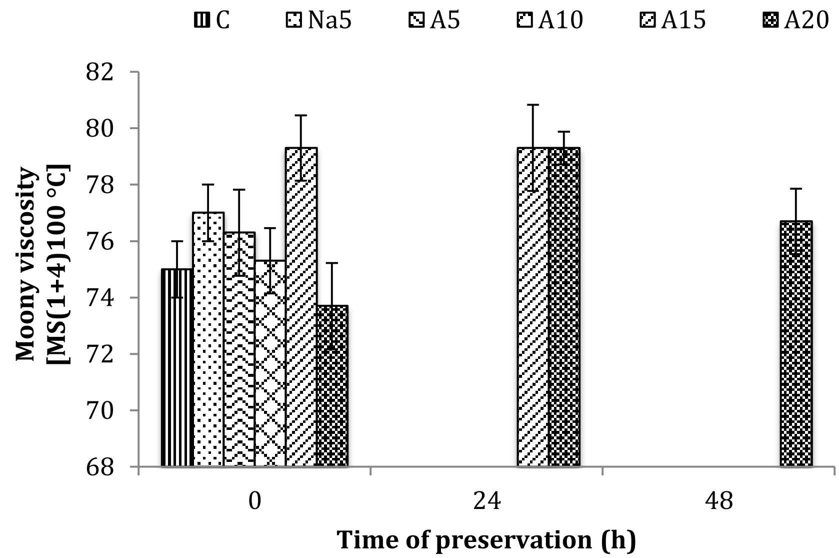

Figure 3. Comparison of Moony viscosity of the different rubber types. Vertical lines indicate the standard error of the means. C = Control, Na5 = Na_2SO_3 (0.05%), A5 = NH_3 (0.05%), A10 = NH_3 (0.10%), A15 = NH_3 (0.15%), A20 = NH_3 (0.20%)

Plasticity retention Index (PRI)

Unaged Rapid Plasticity Number (P_0)

There was no significant difference of P_0 values ($p>0.05$) of the RSS produced from different preservation systems and at different times of preservation (Figure 4). The results clearly showed that the P_0 values of the sheets produced from ammonia-treated latex samples were similar to those of the control even after an increase in the time of preservation.

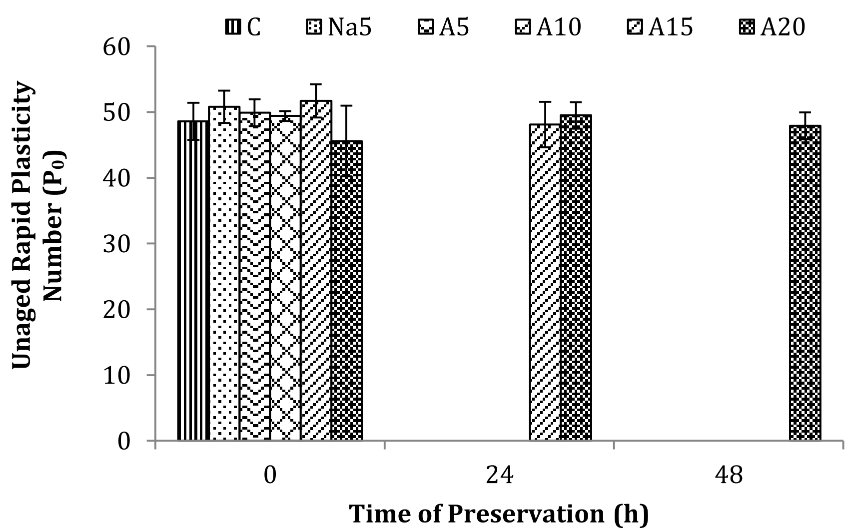

Figure 4. Comparison of Un-aged Plasticity Number of the different sheet rubber types. Vertical lines indicate the standard error of the means. C = Control, Na5 = Na_2SO_3 (0.05%), A5 = NH_3 (0.05%), A10 = NH_3 (0.10%), A15 = NH_3 (0.15%), A20 = NH_3 (0.20%)

Rapid Plasticity Number (P_{30})

Figure 5 illustrates the changes in the rapid plasticity number (P_{30}) of RSS produced from latex preserved with different concentrations of ammonia-treated latex. This general reduction of P_{30} value was observed even with an extended period of preservation. However, the different preservation periods did not have a significant effect on P_{30} ($p>0.05$). The ammonia-treated samples showed a marginal reduction of P_{30} with the increase in concentration of ammonia on latex, compared to that of both control and Na_2SO_3-treated samples. Ammonia may have an adverse effect of the antioxidants present in the natural rubber latex such as Tocotrinols, and could also convert these antioxidants to its salt-form. Nadarajah *et al*. (1972) reported that these salts may leach out during processing. There was a significant effect different preservative systems on the P_{30} value of the samples ($p<0.05$). There was a marginal increase in the P_{30} value of the sheets produced from 0.2% ammonia-treated samples with 48 h keeping time (A20-48). This could be due to an experimental error when producing samples for the PRI test.

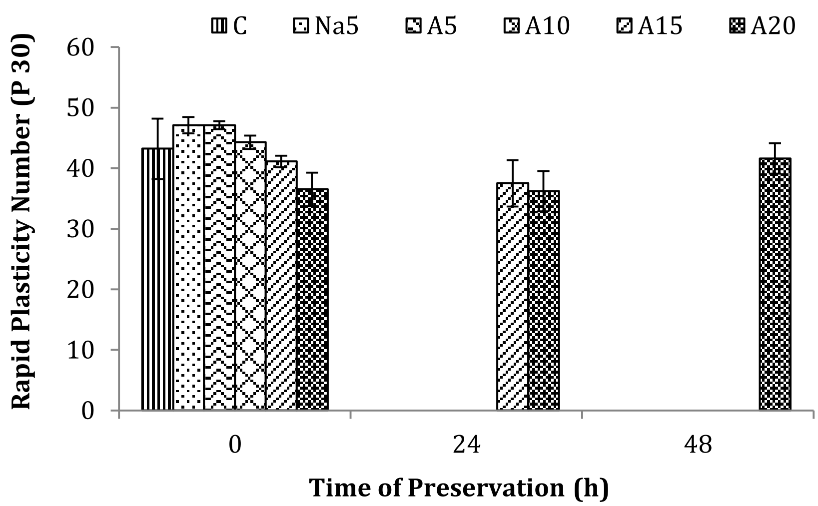

Figure 5. Comparison of the Rapid Plasticity Number of the different rubber types. Vertical lines indicate the standard error of the means. C = Control, Na5 = Na_2SO_3 (0.05%), A5 = NH_3 (0.05%), A10 = NH_3 (0.10%), A15 = NH_3 (0.15%), A20 = NH_3 (0.20%)

Plasticity Retention index (PRI)

The different preservations systems had a significant effect ($p<0.05$) on the plasticity retention index (PRI) of the samples prepared (Figure 6). However, there was a marginal decline of the PRI values with the increase in the ammonia concentration on NR latex. The PRI value is determined as the ratio of P_{30} to P_0 and therefore, the result are as expected, though there was no significant effect of the time of preservation on PRI. However, all sample had PRI values above the recommended PRI value (above 60%) to be uses as an industrial raw material.

Mechanical properties

Some mechanical properties of rubber vulcanizates produced from latex with different preservation histories are given in Table 6. There was a marginal reduction in the tensile properties of ammonia-treated sample compared to that of Na_2SO_3-treated sample ($p>0.05$). However, the aged tensile properties of ammonia-treated samples were significantly reduced ($p<0.05$) compared to those of Na_2SO_3-treated and aged samples. This may be due to the removal of antioxidant as ammonium salts (Nadarajah *et al*., 1972).

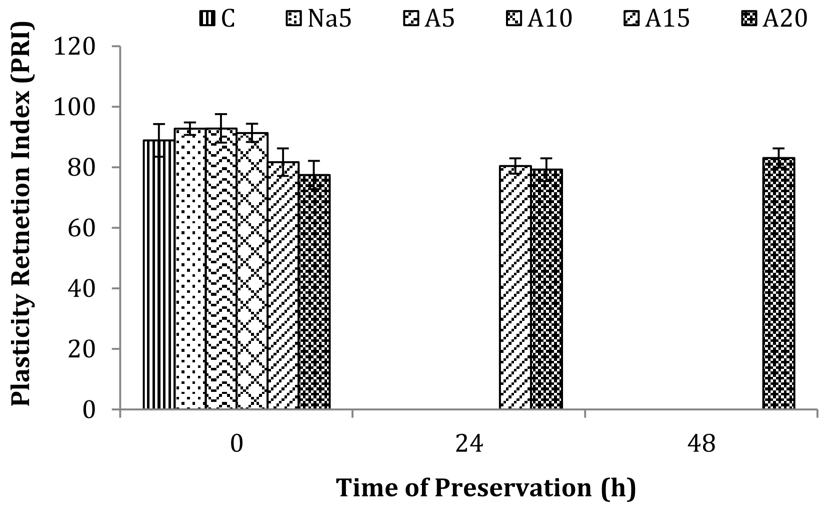

Figure 6. Comparison of Plasticity Retention Index of the different rubber types. Vertical lines indicate the standard error of the means. C = Control, Na5 = Na_2SO_3 (0.05%), A5 = NH_3 (0.05%), A10 = NH_3 (0.10%), A15 = NH_3 (0.15%), A20 = NH_3 (0.20%)

The un-aged and aged tear properties of RSS produced from latex preserved with 0.2% ammonia and 0.05% Na_2SO_3 for less than a day were similar ($p>0.05$; Table 6). However, within the aged category, ammonia preserved latex had a significant impact ($p<0.05$) on the tear properties.. This may also be due to the removal of naturally occurring antioxidants as ammonium salts during processing (Nadarajah *et al.*, 1972). The different preservatives also had a significant effect on the rebound resilience ($p<0.05$), however, the abrasion resistance and hardness were not affected by the preservative system ($p>0.05$) at the un-aged state.

Table 6. Comparison of curing properties of RSS produced from ammonia-treated with sodium sulphite-treated latex

Properties	Preservation system*	Un-aged	Aged
a) Tensile strain (%) at break	Na5-0	380.02	356.97
	A20-24	363.47	263.85
b) Tear (N/mm)	Na5-0	67.691	60.589
	A20-24	63.396	47.066
c) Abrasion resistance (g)	Na5-0	0.0789	-
	A20-24	0.0839	-
d) Hardness (N)	Na5-0	51.3	-
	A20-24	55.2	-
e) Rebound resilience (cm)	Na5-0	61	-
	A20-24	62	-

* Refer to Table 2 for the preservation system codes.

Conclusion

The natural rubber field latex (NRFL) could be preserved and kept for more than two days, provided that the ammonia concentration of the latex exceeds at least 0.15% on latex. Increase in the ammonia concentration would increase preservation time, acid requirement, drying period and the volatile matter content (VMC). The VMC would reduce with the increased time of preservation. The Moony viscosity also increased with the increase in ammonia concentration on latex and the preservation time, resulting in reduction in the aged rapid plasticity number and the plasticity retention index. However, neither the increase in ammonia concentration nor the preservation time had an effect on the unaged rapid plasticity. The mechanical properties such as unaged tensile and tear properties, hardness and abrasion resistance showed similar values in the Ribbed Smoked Sheet (RSS) produced from sodium sulphite-treated natural rubber latex, however, the aged tensile and tear properties, and rebound resilience were reduced when ammonia was used as a preservative.

Acknowledgements

The authors wish to express deepest gratitude to Dr. W. M. G. Senevirantne, the Director of Rubber Research Institute of Sri Lanka for providing a valuable opportunity to conduct the research at RRISL, Agalwatte, Sri Lanka.

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