Raw rubber properties of crepe rubber manufactured from preserved natural rubber latex using different combinations of preservatives

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Abstract

Objective of this study was to investigate the effect of different preservative systems used in the concentrated latex manufacturing industry on physical properties of the latex crepe made out of them. Unfractionated and unbleached (UFUB) crepe rubber manufactured from latices preserved with ammonia, tetramethylthiuram disulphide, zinc oxide and a 1:1 mixture of tetramethylthiuram disulphide (TMTD) and zinc oxide (LATZ) were subjected to examine their raw rubber properties. It was observed that UFUB crepe rubber manufactured out of either ammonia preserved, ZnO preserved or chemically untreated latices have better resistance to thermo-oxidative degradation compared to UFUB crepe rubber made out of both TMTD and LATZ preserved latex. Further, it was observed that neither ammonia nor ZnO has any effect on the thermal degradation of crepes made out of ammonia or ZnO preserved latex. It was clear from the results that the TMTD added as a component of the preservative system adversely affects the resistance to thermo-oxidative degradation as judged by PRI of crepe produced.

Crepe rubber manufactured from TMTD preserved latex exhibits unusually lower PRI and a nitrogen content comparable with the normal UFUB crepe rubber. Skim crepe rubber which is considered a by-product of the latex centrifuging industry, usually records higher nitrogen percentages and lower PRI values. Therefore, evaluation of these two parameters could be used to differentiate skim crepe rubber from normal UFUB crepe rubber. It was also observed that TMTD has a strong negative impact on PRI of crepe rubber even at very low concentrations. It could be proposed that dimethylthiuram monosulphide (DMTMS) free radicals generated by thermal decomposition of TMTD are responsible for this PRI reduction.

Key words: latex preservatives TMTD, raw rubber properties, ZnO

Introduction

Natural Rubber Latex (NRL) exuded from *Hevea* tree is prone to deteriorate in quality due to activity of micro-organisms on non-rubbers present in latex. Therefore, preservation of field latex at the field level is of prime importance to prevent acid development caused by the action of micro-organisms on the carbohydrates present in latex.

Different preservative systems are used in the raw rubber industry to preserve latex. Preservative systems are selected considering the type of raw rubber intended to be produced out of the latex or the duration for which latex is kept for further processing. A summary of preservative systems commonly used in latex industry is given in Table 1.

Na₂SO₃ is used as a short-term preservative in crepe rubber manufacture. Ammonia is used as a sole long term preservative at high concentrations (0.7%) when latex is required to be stored for a few days before further processing. However, use of ammonia at high concentrations has certain disadvantages. Some of them are (i) higher consumption of acid for subsequent coagulation (ii) discoloration of resulting rubber (iii) practical difficulties encountered in handling ammoniated latex at high concentrations (iv) processing difficulties of highly alkaline skim latex (Backely, 1997). Therefore, secondary preservative systems with low ammonia content in latex have been developed for

the preservation of NR latex by *John, et al.* It has become the widely used commercially accepted preservative system in the centrifuged latex industry. This system which is known as LATZ in the industry contains ammonia, tetra methylthiuram disulphide (TMTD) and Zinc Oxide (ZnO) as shown in Table 1. There are instances where inadequately preserved LATZ latex becomes unsuitable for the manufacture of centrifuged latex due to poor latex preservation procedures adopted in the field. In such instances, it is necessary to convert this latex into an alternate form of natural rubber to recover the rubber. Rejected latex is normally converted to crepe laces. Therefore, a study was carried out to investigate the raw rubber properties of crepe rubber manufactured from LATZ preserved field latex with the following objectives.

1. to study raw rubber properties of crepe rubber manufactured using LATZ preserved latex
2. to identify the responsible component/s of the preservative system which affects raw rubber properties of the rubber produced
3. to study the minimum tolerable level of the responsible component/s in the preservative system
4. to elucidate the mechanism of the effect of identified preservative component/s on the raw rubber properties.

Table 1. *Different preservative systems used for NR field latex*

Preservative system	Type of raw rubber	Period of preservation
Na ₂ SO ₃	LCR	< 4 hours
0.7% Ammonia	HACL	> 3 days
0.2% Ammonia + 0.2% boric acid (LA –BA system)	LACL	> 3 days
0.2% Ammonia + 0.1% zinc diethyldithiocarbamate (LA –ZDC system)	LACL	> 3 days
0.2% Ammonia+0.013% tetramethylthiuramdisulphide + 0.013% zinc oxide (LATZ system)	LACL	> 3 days
LCR – latex crepe rubber, HACL – high ammonia centrifuged latex, LACL – low ammonia centrifuged latex		

Materials and Methods

Field latex was obtained from Dartonfield estate, Agalawatta, belonging to the Rubber Research Institute of Sri Lanka. Chemicals used were ammonia, tetramethylthiuram-disulphide (TMTD), zinc oxide (ZnO) and formic acid. All chemicals were industrial grades and were purchased from general chemical suppliers. Ammonia was used as a 10% aqueous solution. ZnO, TMTD and a mixture of 50/50 ZnO/TMTD were used as 50% dispersions in water containing 1% Dispersol LR (a proprietary surfactant). The dispersions were prepared by ball milling the mixture for over 48 hours at room temperature (30 °C).

Determination of acid requirement for overnight coagulation of LATZ preserved latex for the manufacture of crepe rubber samples

Forty litres of field latex having a metrolac reading of 100 (DRC approx. 30) were taken. The latex was diluted

with pure water to reduce the DRC of latex to approximately around 10% which is the standard DRC value for crepe rubber manufacture. It was then divided into five sets of equal volumes. Ammonia and TMTD/ZnO dispersions were added to these samples at dosages shown in Table 2. They were used to establish the acid requirement to bring the pH of the latex to the iso-electric point of NR latex (pH 4.8-4.4) by gradual addition of 1% formic acid. Upon estimation of the formic acid requirements, the latex samples were coagulated by direct addition of respective quantities of 10% formic acid to latex and the samples were kept overnight for complete coagulation.

Determination of the effect of different preservative systems on raw rubber properties

Thirty litres of natural rubber latex were taken from Dartonfield Estate, Agalawatta. They were divided into six portions and preservatives were added as shown in Table 3.

Table 2. *Latex samples used for estimation of optimum acid consumption*

Sample name	NH ₃ concentration of latex % (w/w)	TMTD/ZnO concentration of latex g/L
Z	0.0	1.0
A	0.1	1.0
B	0.2	1.0
C	0.3	1.0
D	0.4	1.0

Table 3. *Preservative systems used for the study*

Sample No	Concentration of ammonia % (w/w)	Concentration of TMTD/ZnO g/L
A00TZ0	0.00	0.00
A01TZ0	0.01	0.00
A05TZ0	0.05	0.00
A10TZ0	0.10	0.00
A00TZ1	0.00	1.00
A20TZ1	0.20	1.00

All samples were coagulated overnight by the addition of appropriate quantities of 10% formic acid as in the previous experiments. These coagulums were then converted to unbleached and un-fractionated pale crepe rubber using standard manufacturing procedures (Tillekeratne *et al.* 2003). Raw rubber properties of crepe rubber samples produced were tested.

Determination of the effect of ZnO on raw rubber properties

Fifty litres of natural rubber latex were taken. They were divided into five portions and ZnO dispersion was added as shown in Table 4 in order to assess the effect of ZnO concentration on the raw rubber properties. Treated latex were mixed well, diluted by adding water 1:1 ratio and samples

were coagulated by addition of 10% formic acid.

Table 4. *ZnO concentrations used*

Sample	ZnO concentration (g/l)
Z0	0.000
Z1	0.125
Z2	0.250
Z3	0.375
Z4	0.500

Determination of the effect of TMTD on raw rubber properties

Fifty litres of natural rubber latex were taken and were divided into five portions. TMTD was added at concentrations shown in Table 5 in order to assess the effect of TMTD concentration on the raw rubber properties of crepe rubber manufactured out of them. Treated latex were mixed well, diluted by adding water at 1:1 ratio. Samples were coagulated by adding 10% formic acid to each sample.

Table 5. *TMTD concentrations used*

Sample	TMTD concentration (g/l)
T000	0.000
T125	0.125
T250	0.250
T375	0.375
T500	0.500

Raw rubber properties

Raw rubber properties of crepe laces were carried out according to the respective ISO standards shown below.

Raw rubber property	ISO test method reference number
Plasticity Number	ISO 2007:1991
Plasticity Retention Index (PRI)	ISO 2930:1995
Nitrogen content	ISO 1656:1996
Ash content	ISO 247:1990
Volatile Matter Content	ISO 248:1991
Mooney Viscosity	ISO 289-1:1994

Results and Discussion**Formic acid requirement for latex coagulation for LATZ preserved latex**

Preliminary trials carried out on coagulation of ammoniated latex have shown that overnight coagulation could be achieved by adjusting the pH range of latex between 4.6-5.07. The acid requirement and corresponding pH values are given in Table 6. Significantly higher quantities of formic acid are necessary for the complete coagulation of ammonia treated latex (10% acid requirement for untreated latex coagulation is approximately 35 ml/kg). As expected, this acid requirement has increased with the increasing concentration of ammonia in latex. However, these acid dosages were used in the experiments to coagulate the ammoniated NR latex samples only. For other samples, normal dosage was used.

Table 6. *The acid requirement and corresponding 10%formic acid requirement*

Sample name	NH3 concentration (%)	TMTD/ZnO concentration (g/l)	Added 10% Formic acid for coagulation (ml)	Final pH	Po	Observations
A	0.1	1.0	1200	5.34	37.5	Coagulation was commenced after about two hours
B	0.2	1.0	2200	5.07	35.3	Coagulation was started after about two hours
C	0.3	1.0	4000	4.6	35.8	Coagulation was started after about two hours
D	0.4	1.0	4440	4.0	44.6	Coagulation was started after about two hours

Raw rubber properties of crepe rubber made out of preserved NR latex

Crepe rubber derived from (i). Preservative free latex (A00TZ0), (ii) three ammonia preserved latex samples with different ammonia concentrations (AXTZ0series), (iii) TMTD/ZnO preserved latex (A00TZ1) and (iv). Low ammonia/TMTD/ZnO (LATZ) preserved latex (A20TZ1) were tested for raw rubber properties. The results are presented in Table 7. It can be seen from the results that raw rubber properties of crepe rubber produced from preservative free latex (control sample) (A00TZ0) are almost similar to that of normal unfractionated and unbleached crepe (UFUB) rubber. This confirms that accepted manufacturing procedures have correctly been

followed for manufacture of crepe rubber samples during this study. Three UFUB Crepe rubber samples manufactured from ammonia preserved latex (A01TZ0, A05TZ0 and A10TZ0) show raw rubber properties are very similar to the properties of the control sample system (A00TZ0). It has been reported that addition of NaOH into natural rubber latex reduces the plasticity retention index of raw rubber produced using the NaOH treated latex (John *et al.*, 1975). However, addition of ammonia has no effect on the raw rubber properties within the ammonia range studied. The results infer that ammonia does not form water soluble complexes with non rubbers present in latex such as antioxidants which affect raw rubber properties like Po and PRI.

Table 7. Raw rubber properties of crepe rubber derived from preserved latex

Sample No	Initial Plasticity (Po)	Plasticity after 30min ageing (P30)	plasticity retention index (PRI)	Mooney viscosity ML (1+4) 100°C	Nitrogen Content % (w/w)	Ash content % (w/w)	Volatile Matter % (w/w)
A00TZ0	42.5 (30 min)	34.2 -	80.47(60 min)	77.0 (75-85)	0.35 (0.6 max.)	0.14 (0.25 ax.)	0.39 (0.5 max.)
A01TZ0	42.4	33.1	78.43	79.0	0.38	0.16	0.37
A05TZ0	44.2	36.2	81.90	79.0	0.35	0.14	0.39
A10TZ0	42.5	32.3	76.00	78.5	0.34	0.14	0.40
A00TZ1	43.5	11.6	26.26	77.0	-	0.19	0.29
A20TZ1	42.3	13.0	30.73	77.5	0.35	0.24	0.43

(---) Standard raw rubber properties of unfractionated unbleached rubber

It can also be shown that coagulation of ammoniated latex using higher acid dosage had no impact on the properties of the rubber produced out of them. It is known that use of higher acid dosages for quick coagulation affects the properties of the rubber manufactured. Excess acid added to latex to neutralize ammonia present in the latex, probably may not involve in the coagulation of latex. Other two crepe rubber samples (A00TZ1 and A20TZ1) which were manufactured using TMTD/ZnO treated latex show a marked reduction of P_{30} and PRI values. However, other properties were not affected by this preservative system.

Therefore, these results confirmed that TMTD/ZnO dispersion available in the composite preservative system is responsible for the drop in PRI of the crepe rubber manufactured using LATZ treated latex. These results are in accordance with the reported PRI values for TSR L and CV grades of TSR manufactured using LATZ preserved latex by (John *et al.*, 1975). Comparison of the PRI values of crepe rubber laces manufactured using TMTD preserved latex and the results reported for TSR grades show that the effect of LATZ on the reduction of PRI is higher for crepe rubber. It is reported that ZnO and TMTD could easily react to form Zn^{2+} dimethyldithiocarbamate (ZDMDC) at high temperatures (Jarrijon, 1946). Therefore, the observed degradation may have been due to

TMTD, ZnO or ZDMDC. However, attention has not been paid to find the responsible component of the LATZ system for the reduction of PRI of rubber. The next sets of experiments were therefore, carried out to find out the responsible component of TMTD/ZnO system which causes the reduction of PRI values.

Raw rubber properties of crepe rubber made out of NR latex treated with ZnO

Crepe rubber made out of ZnO treated latex was tested for some of the raw rubber properties (P_0 , PRI & VR) which are supposed to be affected when a rubber is subjected to a degradation process. The results are presented in Table 8. It can be seen from the results that ZnO does not affect raw rubber properties significantly. PRI values of crepe rubber manufactured from ZnO treated latex does not significantly deviate from that manufactured from untreated latex which indicates that incorporation of ZnO at the latex stage does not initiate or catalyze degradation of rubber molecules. This is again confirmed by the value of Mooney viscosity of the treated crepe rubber when compared with that of the control sample (Z0). Drop of PRI of a rubber could also be due to metal ion catalyzed oxidation of the main chain. Most responsible ions are Fe, Cu and Mn (Ratnayake *et al.* 2011). However, these results reveal that ZnO used in this

experiment do not even have such metal ions as contaminant at appreciable levels to affect any degradation process of rubber. The study was then extended to investigate the effect of incorporation of TMTD at latex stage on the raw rubber properties of crepe rubber.

Raw rubber properties of crepe rubber derived from NR latex treated with TMTD

Five latex samples treated only with different concentrations of TMTD were prepared and tested for Po, PRI, Mooney viscosity and molecular weight measurements of the crepe rubber made out of TMTD incorporated latex. The results given in Table 9 clearly show that TMTD is the responsible component in the LATZ composite preservative system for the reduction of the resistance to oxidation of crepe rubber as assessed by PRI values. It could also be seen that increasing concentration of TMTD has decreased

the PRI value. This observation again confirmed the involvement of TMTD in reduction of the PRI of raw rubber. No minimum quantity that could be added to latex without affecting the PRI value was found within the TMTD range (preservable range) studied. It has been reported that PRI values of skim crepe rubber which is produced from skim latex generated during the centrifuged latex manufacturing process using Ammonia/TMTD/ZnO preserved latex are also low similar to PRI values of raw rubber produced from TMTD treated latex. However, skim laces show very high nitrogen content when compared with the average nitrogen content of normal crepe rubber (Anon, 2008) (Table 10). Therefore, the comparison of nitrogen content of crepe laces together with PRI values could be used to differentiate the crepe rubber made out of TMTD added latex from skim latex crepe.

Table 8. *Raw rubber properties of crepe rubber manufactured out of ZnO treated latex*

Sample	Po	P30	PRI	Mooney viscosity ML (1+4) 100 °C	Nitrogen content % (w/w)
Z0	39.8	31.8	80	69.0	0.31
Z1	40.2	35.1	87	71.0	0.32
Z2	40.1	35.3	88	70.0	0.35
Z3	40.7	35.1	86	67.0	0.34
Z4	39.2	33.3	84	67.0	0.32

Table 9. *Some properties of crepe rubber derived from TMTD treated latex*

Sample	Po	P30	PRI	Mooney viscosity ML (1+4) 100°C	Molecular weight by viscosity measurements 10 ⁶ g/mol	
					MW1	MW2
T0	40.6	29.4	72.41	71.0	1.4289	1.8915
T125	41.6	21.5	51.68	71.0	1.4773	1.9700
T250	40.9	8.5	20.78	69.5	1.1876	1.0619
T375	41.0	*	-	69.0	1.1501	1.1248
T500	40.6	*	-	68.5	1.0472	0.8953

* Samples got melted

MW1 Graphs plotted manually

MW2 Graphs plotted using GNU Plot software package

Table 10. *Raw rubber properties of skim rubber [10]*

Sample	P0	PRI	Nitrogen content% (w/w)
1	49.5	47.2	0.9
2	40.3	20.5	0.72
3	45.9	15.9	1.73

It has been reported in literature that TMTD could act as a pro-oxidant other than acting as a bactericide or a rubber vulcanizing accelerator for NR latex (Debapriya *et al.*, 2006; Bevilacqua, 1959). The effect of TMTD on PRI is clearly elucidated from the results presented in Table 9. It is interesting to note that Po which is a measure of plasticity or flowability of rubber has not been affected when the rubber samples were subjected to a compression without prior heating during the estimation of the value.

When the samples were heated for thirty minutes at 140±0.2°C before compression at 100 °C for the estimation

of P₃₀, rubber has degraded as reflected by the very low P₃₀ values of the samples containing higher TMTD concentrations (T3 and T4 samples). Therefore, it could be inferred from these results that TMTD is responsible for initiation or propagation of chain scission or thermal oxidation of NR under high heat. It can also be seen that Mooney viscosity values have also shown a slight decreasing trend with the increasing concentration of the TMTD suggesting a TMTD accelerated degradation of NR molecules.

Molecular weight measurements are also shown a gradual decrease in their molecular weight with increasing

TMTD concentration. Debapriya *et al.*, 2005 explained that TMTD breaks polymer chains and crosslink bonds simultaneously with breaking of TMTD to form thiocarbamate radicals (Debapriya *et al.*, 2006). All these observations confirm that TMTD is the material responsible for the reduction of PRI value of rubber. It could be pure TMTD, or derivative or intermediate product of TMTD or metal ions present as contaminants in TMTD which are responsible for this molecular breakdown.

It was reported in literature that TMTD, in the presence of ZnO could form Zinc dithiocarbamate. This is not a matter of concern as the TMTD even in the absence of ZnO, causes degradation of NR. TMTD could be transformed to corresponding mono-sulphides with the

liberation of one atom of active sulphur from each molecule of disulphide (Debapriya *et al.*, 2006; Bevilacqua, 1959). It is known that free sulphur influences modifications in the main chain in many ways (formation of mono and dicyclicsulphidic attached group and transformation of cis-trans isomerism) in the rubber vulcanizate (Robert, 1988). Similarly, free sulphur if generated, may initiate a molecular degradation process in the absence of other cross-linking agents. TMTD has a sulphur-sulphur bond which is thermally weaker bond than the carbon-carbon or carbon-sulphur bonds. Therefore, there is a possibility of initiating two dimethyl thiurammono-sulphide free radicals under heat which can subsequently initiate the chain scission reactions as proposed below.

It has been reported that TMTD is an effective multifunctional reclaiming agent. Even though bond strength of central S-S bond of aliphatic disulphide which is in the order of -70 kcal/mol is high for appreciable thermal dissociation into radicals at moderate temperatures (Debariya *et al.*, 2006), it is reported that potential resonance stabilization of the radicals may apparently weaken the central bond in thiuramdisulphide and favour the formation of the thiocarbamate radical. Therefore, further studies should be carried out to understand the mechanism of degradation of rubber molecules of the rubber manufactured out of TMTD incorporated NR latex.

Conclusions

Among the three chemicals, viz. ammonia, ZnO, TMTD, commonly used for preservation of NR latex, it was found that neither ammonia nor ZnO has any influence on the thermal degradation of rubbers. However, it was found that TMTD has a strong influence on thermal degradation of rubber as indicated by the low PRI values of crepe rubber produced. Nevertheless, TMTD has no effect on Initial Wallace plasticity (P_0) and other raw rubber properties such as dirt content, VM, Nitrogen content, ash content and Mooney viscosity. It was also observed that more the TMTD concentration in latex lower the PRI values of the raw rubber manufactured. It can be

concluded that extremely high nitrogen content together with low PRI could be an indication to identify the crepe rubber made out of skim latex while both low nitrogen content and low PRI values could be used to identify the crepe rubber made out of TMTD treated field latex or latex concentrate.

References

- Anon (2008). Sample analysis report, Raw Rubber & Chemical Analysis Department, RRISL, 2008.
- Bevilacqua, E M (1959). *Rubber Chemistry and Technology* **32**, 721-737.
- Blackley, D C (1997). Polymer lattices. *Science and Technology*, 2nd edition. Vol.2. *Types of Lattices*. pp.27-40.
- Debapriya De, Amit Das, Debasish De, Brojenctranath Dey, Subhas Chandra Debhath, Bidhn Chandra Roy (2006). Reclaiming agent. *European Polymer Journal* **42**, 917-927.
- Jarrijon, A (1946). Application of Ultraviolet Spectroscopy: A study of the transformation which tetramethylthiuram disulphide undergoes during the vulcanization process. *Rubber Chemistry Technology* **19**, 1061-1076.
- John, C K, Nadarajah, M, Rao, P S R, Lau, C M and NG, C S (1975). A composite preservation system for *Hevea* latex. *Proceedings of the International Rubber Conference*, Kuala Lumpur, 1975.
- Ratnayake, U N, Sarath Kumara, P H, Siriwardene, T A S, Prasad, A K D W and Rohanadeepa, V C (2011). Effect of iron in processing water on quality of crepe rubber. *Journal of the Rubber Research Institute of Sri Lanka* **91**, 1-14.

Roberts, A D (1988). *Natural Rubber Science and Technology*. Oxford University Press.

Tillekeratne, L M K, Nugawela, A and Seneviratne, W M G (2003). *Handbook of Rubber*, Vol. 2. *Processing*. Rubber Research Institute of Sri Lanka, Dartonfield, Agalawatta, Sri Lanka 191 pp.

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