

QUALITY PARAMETERS OF SOME NATURAL RUBBER (NR) CLONES INDIGENOUS TO NIGERIA. II. IONIC CONTENT, STABILITY AND DEGRADATION RESISTANCE OF NATURAL RUBBER

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(Received 4 March 2000; accepted 24 June 2002)

The degradation resistance, protein content and the ionic analysis of the lattices of two local natural rubber (NR) clones (NNRL-Ilawe Ekiti) and NNRG-Igede Ekiti) and an international natural rubber clone (TJI-Malaysia) have been studied. The international clone (TJI) was observed to be more resistant to oxidative degradation than the local clones. The resistance of NR to oxidative breakdown was improved by oxalic and phosphoric acid additives and was found to be related to absolute temperature by an Arrhenius type of equation thereby allowing for the evaluation of the activation energy which is taken to be a measure of the degradation resistance of NR. The lattice of the international clone (TJI) appears superior to the lattices of the local clones examined, being of higher protein content, stability and degradation resistance.

Key words: Natural Rubber, Degradation resistance, Protein content, Ionic analysis.

Introduction

In an attempt to establish the quality of our local natural rubber lattices, some workers examined the dry rubber content and the protein content of some local natural rubber lattices (Ajayi and Malomo 1992a; Ajayi *et al* 1992b). The relative quality of the compounds and the vulcanizates produced from the lattices of some natural rubber indigenous to Nigeria and those of an international clone has been studied (Adu and Adeosun 1997). The results of these studies establish no appreciable superiority of the international clone over the local clones studied.

Just like the compounds of natural rubber are manipulated into many useful products (tyres, shoe soles, carpets etc.), the lattices are used direct in the manufacture of many products like foam mattresses, gloves and disposable syringes. The processing of these materials is dependent on the stability and the ionic content of the lattices. The ionic content of latex is, therefore, of continuing interest since it is believed to contribute to the properties and especially the processing of the latex. The control of the shear stability and viscosity characteristics of the latex compound are believed to relate at least partly to the ions naturally present in it. In modern latex processing, large-scale production plants require consistent and high quality processing characteristics from natural latex

and so this subject of ion levels is considered of special technological importance (Crafts *et al* 1984). It has been reported that latex, just like many other natural products contains many naturally occurring inorganic elements and that the quality of the latex is a function of these elements (Bateman and Sekhar 1966). Cu, Mn and Fe are known to be prooxidants or catalysts and they promote the oxidative degradation of rubber. In addition, information on contents of such trace elements especially Cu has relevance to the contamination of rubber from fungicides containing metals. Nitrogen content of rubber gives an indication of the total amount of proteins in the rubber. The contribution of proteins to the general colloid stability of latex and its ageing properties has been demonstrated (Yip 1990; Hasma and Alias 1990). Analysis of other elements such as K, Na, Ca and P are also important when one is interested in the nutritional and physiological studies of rubber tree and the quality of latex (Belmas 1949). Crafts *et al* (1984) also reported the presence of carbonate, phosphate, sulphate, chloride, oxalate, acetate, formate, amino, acids and proteins in natural rubber latex.

The properties of the compounds and the vulcanizates of two local clones (NNRI-Ise-Ekiti) and (NNRO-Okipupa) have been compared with those of an international clone (RRIM 600) cultivated in Nigeria (Adu and Adeosun 1997). No appreciable superiority of the international clone was es-

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established over the local clones. In this work the ionic content, protein content and the degradation resistance of the lattices of two other local clones cultivated in Ekiti-State (NNRL and NNRG) have been studied alongside those of another international clone (TJI). The effect of some processing chemical on the degradation resistance of the lattices was also examined.

Experimental

Source of lattices: Natural rubber lattices were collected from Ilawe-Ekiti (NNRL), Igede Ekiti (NNRG) and Federal College of Agriculture, Akure (TJI). A portion of the lattices was used for ionic content determination. The other portion was allowed to coagulate and processed into primary product (crumb).

Plasticity retention index: This was determined at the Michelin quality control laboratory, Araromi-Obu, Ondo-state using the standard method described elsewhere (RRIM 1970).

Elemental and anion analysis: Sodium and potassium were determined by a flame photometer technique while the other minerals were determined by AAS technique (AOAC 1980). The anions were also determined as described by Craft *et al* (1984). Protein content was determined using the Kjeldahl method (AOAC 1980).

Mathematical treatment of data: The temperature dependence of plasticity retention index (PRI) fitted with the Arrhenius type of equation from where the activation energy ΔE_d of degradation was evaluated.

$$[PRI] = A \exp \frac{\Delta E_d}{RT}$$

where

R = general gas constant

T = absolute temperature

The plot of log (PRI) versus inverse absolute temperature $[1/T]$ showed a straight line from where the activation energy of degradation ΔE_d was evaluated as the slope of the straight line.

Results and Discussion

The percentage crude protein of both local and the international clones are shown in Table 1. The value of NNRG (local clone cultivated in Iged, Ekiti State, Nigeria) though low (3.80) is comparable to those obtained for RRIM 600, an international clone with a value of 3.54 and another local clone, both cultivated in Benin City, Nigeria (Ajayi *et al* 1992b). It is observed that the protein content of the international clone

Table 1
Percentage protein contents of the rubber clones

	TJI	NNRL	NNRG
1	6.72	4.70	3.78
2	6.70	4.74	3.80
3	6.1	4.72	3.82
Mean	6.1	4.72	3.80

TJI, International clone; NNRL, Nigerian local clone from Ilawe, Ekiti-State, Nigeria; NNRG, Nigeria local clone from Igede, Ekiti - State, Nigeria

Table 2
Analysis of the lattices

	NNRL	NNRG	TJI
Na (ppm)	31.54	27.92	46.05
K (ppm)	179.80	128.27	236.34
Mn (ppm)	1062.50	715.50	504.50
Cu (ppm)	57.80	48.86	37.50
Fe (ppm)	23.05	14.09	31.61
Sulphate (%)	7.89	0.55	0.16
Chloride (%)	0.11	0.08	0.77
Phosphate (%)	0.08	0.05	0.03

NJI (of Malaysian origin) is higher than those of the two local clones (NNRG) and (NNRL) of Nigerian origin examined. This observation may be attributed to the near non-existence of agronomical practices in the plantations where the local clones are cultivated an poor plant mechanism for uptake of nitrogenous nutrients of the local clones. The role of certain leguminous plants found in the TJI plantation in nitrogen fixation in the nodules of these legumes may be aiding the soil nitrogen content and hence the uptake of nitrogen. The high protein content of TJI is an advantage in processing especially in processes involving the exposure of latex to the atmosphere, requiring latex with high stability, protein being capable of acting as a heat fugitive and additional crosslink agent for rubber (Hasma and Alias 1990).

The ionic contents of the lattices examined are shown in Table 2. The potassium content just like the nitrogen content follows the decreasing trend TJI, NNRL and NNRG. This might be due to fertilizer application effected in the TJI plantation which is not done in the plantations where the local clones are cultivated. The sodium content is also highest for TJI like potassium. Both are associated with almost every important physiological process in plant metabolism suggesting that the yield of TJI clone would be higher than for the local clones. The percentage phosphate and sulphate are lowest for the TJI clone which is an advantage for high content of both ions

Table 3
Plasticity retention index (PRI) of natural rubber clones and their additives with oxalic and phosphorous acids as a function of temperature

Cure time (min)	Cure temperature (k)	10^4 (K ⁻¹)	Log (PRI)				
			TJI	NNRL	NNRG	NNRL with oxalic acid	NNRG with phosphorus acid
30	373	2.61	1.90	1.88	1.87	1.95	1.95
30	393	2.55	1.86	1.85	1.85	1.90	1.89
30	398	2.51	1.85	1.85	1.84	1.88	1.86
30	403	2.48	1.77	1.76	1.76	1.79	1.78
30	413	2.42	1.75	1.74	1.74	1.76	1.76

decreases natural rubber stability (Crafts *et al* 1984). Copper and manganese ions which are known to promote oxidative degradation of rubber show the decreasing trend NNRG, NNRL and TJI connoting that the lattices of the local clones would be more prone to oxidative degradation than the NJI clone.

The plasticity retention index (PRI) which is a measure of resistance to oxidative degradation (RRIM Bull 1970) of the natural rubber clones examined are shown in Table 3. Generally the PRI of the international clone TJI seems higher than the PRI of the local clones connoting that the TJI clone has a

higher ability to resist oxidative degradation than the local clones examined. The variation of PRI with absolute temperature as shown in Table 3 fitted the Arrhenius equation of the type mentioned earlier. The plots of log PRI versus inverse absolute temperature (Fig 1) show linearity from where the activation energy of degradation ΔE_d was evaluated (Table 3). It is observed that the activation energy of degradation follows the decreasing trend TJI, NNRL and NNRG, which is in agreement with the resistance to oxidative degradation (PRI) trend. It seems that the higher is the activation energy of degradation, the higher is the resistance to degradation.

An attempt was made to boost the degradation resistance of the local clones by adding oxalic acid and phosphoric acid separately to the natural rubber lattices of the local clones. As shown in Table 3, both acids enhanced the PRI and the activation energy of degradation of the local rubber clones.

Conclusion

Results show the international clone TJI to be more resistant to oxidative degradation than the local clones examined. The plasticity retention index of natural rubber was found to be related to absolute temperature by an Arrhenius type of equation that allows for the evaluation of the degradation resistance of natural rubber in terms of activation energy of degradation. The degradation resistance of the local clones was enhanced by oxalic and phosphoric acids.

The international clone, being of higher protein content, stability and degradation resistance relative to the local clones, appears superior in quality to the local clones. The degradation resistance, the protein content and the stability of the local clones could however be enhanced by the application of oxalic and phosphoric acids to their lattices and NPK fertilizer to the soil on which they are cultivated.

References

- Adu O E, Adeosun B F 1997 Quality parameters of some NR clones indigenous to Nigeria. *J Technoscience* **1** (1)5.
- Ajayi J D, Malomo D 1992a The dry rubber content (dre) of some Nigerian wild rubber Heave. *Nigerian J Sci Tech* **5** (1) 54-56.
- Ajayi J D, Malomo D, Simire J O P 1992b Protein content of some Nigerian natural rubber lattices. *NJST* **5** (1)57-58.
- AOAC 1980 In: *Official methods of analysis*. 13th ed. Washington D.C.
- Bateman L, Sekhar B C 1966 Significance of PRI in raw rubber and vulcanized natural rubber. *J Rub Res Inst Malaya* **19**(3) 133.
- Belmas R 1949 Contribution to the physico-chemical study

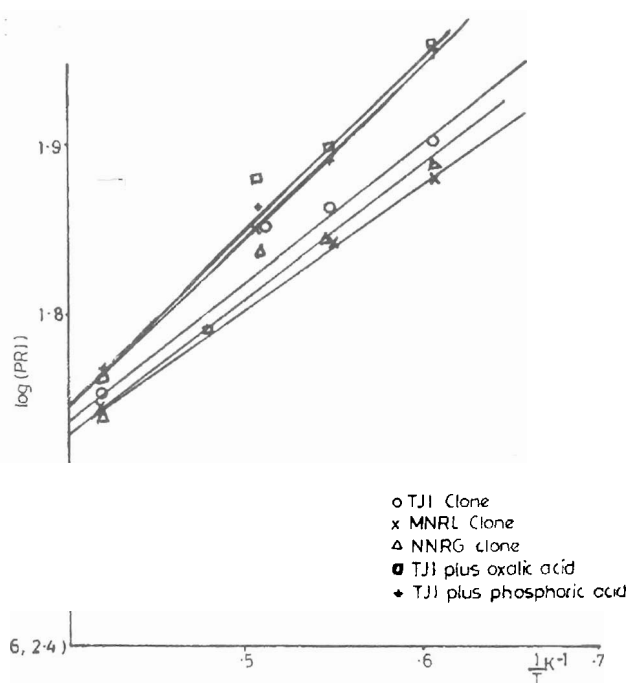


Fig 1. Plot of log (PRI) versus inverse absolute temperature for natural rubber and natural rubber/chemical additives.

- of Hevea latex. *Revue Gen Caoutch* **26** 341.
- Crafts R C, Gorton A D T, Pendle T D 1984 The effects of anions on some properties of natural rubber latex concentrate. *Conference Paper International Rubber Conference, Moscow*.
- Hasma H, Alias B O 1990 Role of some non-rubber constituents in thermal oxidation ageing of NR. *J Nat Rub Res* **5**(1) 1-8.
- Prim 1970 Test methods of standard Malaysian rubber. *SMR Bulletin No.7*.
- Yip E 1990 Clonal characterization of latex and rubber properties. *J Nat Rub Res* **5**(1) 52-80.