Research Article / Review Article

FUPRE JOURNAL 10(1):109-119(2026)
https://doi.org//10.60787/FJSIR.v10i1.109-119

FUPRE Journal
of
sScientific and Industrial Research

ISSN: 2579-1184(Print) ISSN: 2578-1129 (Online)

http://fupre.edu.ng/journal

Comparative Study of Phenol-Based Oxidative Discoloration in Natural Rubber Properties

***OKUNZUWA, I. G.*[1,*], *APO, P. T.*[2]**

[1,2]*Department of Chemistry, Faculty of Physical Science, University of Benin, Benin city, Nigeria.*

ARTICLE INFO

Received: 01/04/2026
Accepted: 18/06/2026

Keywords

Hevea brasiliensis, Natural rubber, Oxidative discoloration, Phenolic compounds, Plasticity retention index, Physicochemical properties

ABSTRACT

Natural rubber is an important industrial biopolymer widely used in the manufacture of tyres, medical products, and engineering materials due to its excellent elasticity and mechanical strength. However, oxidative discoloration caused by naturally occurring phenolic compounds in latex can influence the quality and stability of raw rubber during processing and storage. This study investigated the effect of phenol-based oxidative discoloration on selected physicochemical properties of natural rubber obtained from Hevea brasiliensis latex. Fresh latex samples were collected from the Rubber Research Institute, Benin City, Nigeria, and analyzed using standard ISO procedures. The evaluated parameters included dirt content, volatile matter, ash content, nitrogen content, initial plasticity (P_0), plasticity after ageing (P_{30}), and plasticity retention index (PRI). The results showed that dirt content ranged from 0.02–0.04%, volatile matter from 0.60–0.67%, ash content from 0.22–0.24%, and nitrogen content from 0.22–0.24%. The P_0 values ranged between 51–56, while P_{30} values ranged from 43–47. PRI values ranged from 78–82%, indicating good oxidative stability of the rubber samples. Samples affected by oxidative discoloration showed slightly higher volatile matter and lower PRI values compared to the control sample, suggesting minor reductions in thermal and oxidative stability due to phenolic oxidation reactions. Despite these variations, all samples remained within acceptable industrial standards for technically specified natural rubber. The study concludes that phenol-based oxidative discoloration exerts only minimal influence on the overall physicochemical quality of natural rubber, although slight reductions in oxidative stability may occur. The findings provide useful information for improving quality control, storage, and processing conditions in natural rubber production.

1. INTRODUCTION

Natural rubber (NR) remains one of the most commercially important biopolymers due to its exceptional elasticity, resilience, tensile strength, and abrasion resistance. It is primarily obtained from the latex of Hevea brasiliensis and consists mainly of cis-1,4-polyisoprene together with minor quantities of proteins, lipids, carbohydrates, phospholipids, and inorganic constituents (Bokobza, 2019). Owing to its unique strain-induced crystallization behavior, NR continues to be indispensable in the manufacture of tyres, medical devices, adhesives, engineering products, aerospace materials, and several industrial components where synthetic rubbers cannot fully substitute its performance characteristics (Wang *et al.*, 2023).The economic importance of NR has continued to increase globally because of the growing demand for high-performance elastomeric

*Corresponding author, e-mail: iyobosa.iyawe@uniben.edu, praiseapo2021@gmail.com
https://doi.org/10.60787/FJSIR.v10i1.109-119
©Scientific Information, Documentation and Publishing Office at FUPRE Journal

materials. Countries in Southeast Asia, Africa, and South America dominate commercial production, with latex harvesting providing livelihood opportunities for millions of people worldwide (Krishnan *et al*., 2019). Although several rubber-producing plant species exist, including *Parthenium argentatum*, *Taraxacum kok-saghyz*, and *Ficus carica*, Hevea brasiliensis remains the principal industrial source because of its superior latex yield and high rubber hydrocarbon content (Omar *et al*., 2024).

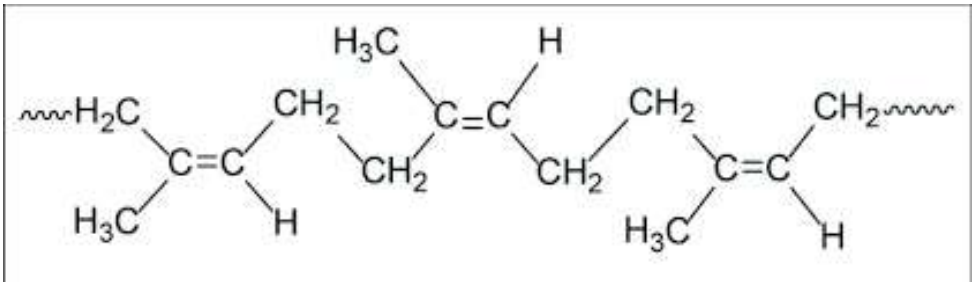


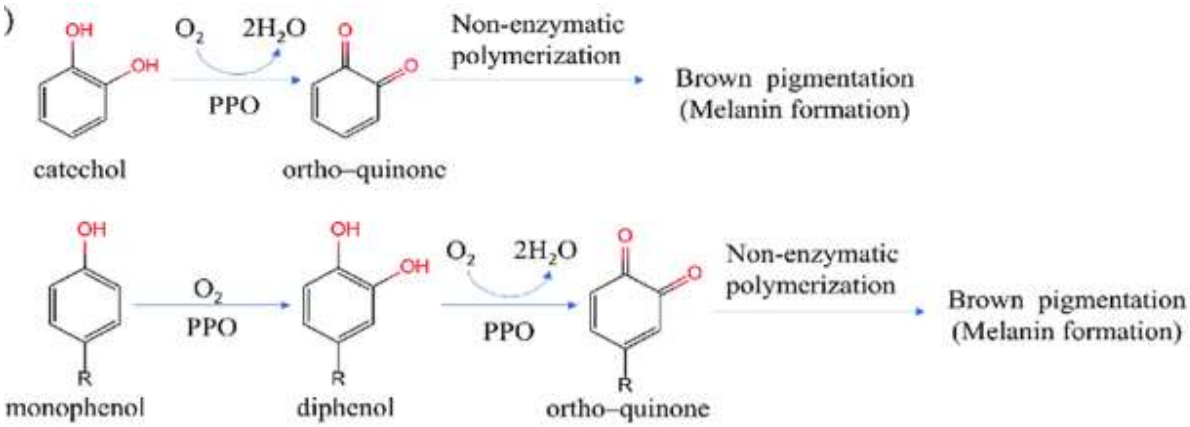
Fig. 1: General chemical structure of Natural Rubber

Despite its industrial significance, the quality of NR is strongly influenced by the presence of non-rubber constituents naturally occurring in latex. These include proteins, amino acids, phospholipids, carbohydrates, metallic ions, and phenolic compounds, many of which participate in oxidation reactions during latex processing and storage (Siriwong *et al*., 2015). Among these constituents, phenolic compounds have attracted increasing scientific attention because of their involvement in oxidative discoloration, a phenomenon responsible for the gradual darkening of raw rubber during handling, coagulation, drying, and storage. Oxidative discoloration in NR primarily occurs through enzymatic and non-enzymatic pathways. In the enzymatic mechanism, naturally occurring phenolic substrates such as catechins, tyrosine, chlorogenic acid, caffeic acid, and dihydroxyphenylalanine (DOPA) are oxidized by polyphenol oxidase (PPO) to form o-quinones, which subsequently polymerize into melanin-like pigments responsible for brown or black coloration (Karunarathne, 2018; Lv *et al*., 2022). PPO enzymes are compartmentalized within specialized organelles such as Frey-Wyssling particles and lutoids in fresh latex. However, mechanical disruption during tapping and processing causes enzyme–substrate interaction, thereby accelerating discoloration reactions (Surani and Sagari, 2021). In addition to enzymatic oxidation, several non-enzymatic reactions contribute to color deterioration in NR. These include lipid peroxidation, photochemical oxidation, Maillard reactions between reducing sugars and amino acids, and metal-catalyzed oxidative processes (Lv *et al*., 2022). Exposure to oxygen, ultraviolet radiation, elevated drying temperatures, prolonged storage, and contamination with transition metals such as iron and copper further intensify pigment formation and oxidative degradation. Such reactions not only affect the visual appearance of NR but may also influence important physicochemical and mechanical properties associated with industrial quality. Colour is an important quality parameter in the grading and commercial valuation of NR. Light-colored rubber grades are particularly preferred for the manufacture of medical gloves, transparent or light-colored rubber goods, adhesives, and specialty elastomeric products because they possess superior aesthetic and processing qualities (Mingzhe *et al*., 2022). Consequently, discoloration

significantly reduces market value and limits the suitability of NR for premium applications. Previous studies have shown that oxidative degradation associated with phenolic compounds may alter properties such as plasticity retention, elasticity, oxidative stability, and storage performance (Rojruthai *et al*., 2021).



Fig. 2: Rubber trees during tapping process



Fig, 3: Pathway diagram from Phenolic compound to Melanin-type pigment

Several analytical parameters are commonly employed to evaluate raw rubber quality and oxidative stability. These include dirt content, volatile matter, ash content, nitrogen content, initial plasticity (P_0), plasticity after accelerated ageing (P_{30}), and plasticity retention index (PRI). Dirt and ash contents provide information on contamination and inorganic residues, while volatile matter reflects moisture and low-boiling components capable of promoting degradation reactions. Nitrogen content is often associated with protein concentration and non-rubber organic matter, whereas P_0 and PRI are important indicators of molecular integrity and oxidative resistance in raw rubber (ISO 247:2006; ISO 248-1:2011; ISO 2930:2019). Although previous investigations have examined oxidative degradation and discoloration in NR, comparatively limited studies have focused specifically on phenol-based oxidative discoloration and its direct relationship with selected raw rubber properties. Understanding this relationship is important for improving processing conditions, minimizing quality

deterioration, and enhancing the suitability of NR for high-value industrial applications. Therefore, this study investigates the comparative influence of phenol-based oxidative discoloration on selected physicochemical properties of natural rubber obtained from Hevea brasiliensis latex. The study specifically evaluates dirt content, volatile matter, ash content, nitrogen content, initial plasticity (P_0), plasticity after thermal ageing (P_{30}), and plasticity retention index (PRI) using standardized ISO analytical procedures.

2. MATRIALS AND METHODS

2.1 Sample collection

Fresh natural rubber latex was obtained from *Hevea brasiliensis* trees at the Rubber Research Institute of Nigeria (RRIN). Iyanomo, Benin City, Edo State The latex samples were collected shortly after tapping and categorized based on visible discoloration. Three samples of which sample 401 and sample 403 showing varying degrees of oxidative discoloration were labeled, while an undiscolored sample 404 served as the control. All reagents used for analysis were of analytical grade and included distilled water, toluene, and other standard laboratory chemicals.

2.2 Sample Preparation

The collected latex samples were processed into ribbed smoked sheets (RSS) following standard procedures in accordance with SAR (Standard African Rubber). Coagulation was achieved using dilute acid, after which the coagulated rubber was passed through rollers to remove excess water and form sheets. The sheets were then air-dried and smoked under controlled conditions to obtain dried rubber samples suitable for physicochemical analysis. Each sample was cut into small pieces prior to testing to ensure uniformity.

2.3 Determination of Dirt Content

Dirt content was determined using the gravimetric method in accordance with SAR (Standard African Rubber) specifications for natural rubber (ISO, 2017; ASTM, 2013). A known weight of rubber sample was dissolved in toluene and filtered through a pre-weighed filter paper. The residue retained on the filter paper was washed, dried, and weighed. The dirt content was calculated as the percentage of insoluble residue relative to the original sample weight.

$$\text{Dirt Content (\%)} = \frac{W2 - W\text{filter}}{W1} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{eq 1}$$

2.4 Determination of Volatile Matter

Volatile matter content was determined by oven-drying This method follows standard procedures for natural rubber analysis. (ISO, 2017; ASTM, 2013). A known weight of rubber sample at 105°C for two hours. After drying, the sample was cooled in a desiccator and reweighed. The percentage weight loss was recorded as the volatile matter content.

$$\text{Volatile Matter (\%)} = \frac{D2 - D3}{D2 - D1} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\

C_3 = crucible + ash.

2.6 Determination of Nitrogen Content

Nitrogen content was determined using the Kjeldahl method. The rubber sample was digested with concentrated sulfuric acid in the presence of a catalyst. The digest was neutralized and distilled, and the liberated ammonia was collected and titrated. The nitrogen content was calculated from the titration values obtained. (AOAC, 2016).

$$\%N=\frac{(Vs-Vb)\times N\times 14.007}{Ws}\times 100$$

……. Eq 4

where Vs= titrant volume for sample (mL),

Vb = titrant volume for blank (mL),

N = normality of acid, and

Ws = sample weight (mg).

2.7 Determination of Plasticity (P_0 and P_{30})

Initial plasticity (P_0) was measured using a Wallace plastimeter. A rubber test piece was placed between heated plates and compressed for a fixed time. The thickness reduction was recorded as the plasticity value. For plasticity after 30 minutes (P_{30}), the sample was subjected to thermal aging at 140°C for 30 minutes before measurement. (ISO, 2020)

2.8 Determination of Plasticity Retention Index (PRI)

The Plasticity Retention Index (PRI) was calculated to determine resistance to thermal oxidative degradation. PRI was computed using the relationship: (ISO, 2020)

$PRI = (P_{30} / P_0) \times 100$

Where:

P_0 = Initial plasticity

P_{30} = Plasticity after 30 minutes of thermal aging

Higher PRI values indicate better resistance to oxidative degradation and improved stability of the rubber sample.

2.9 Statistical Analysis

All measurements were carried out in triplicate, and average values were recorded. The results obtained for discolored samples were compared with the undiscolored control to evaluate the effect of oxidative discoloration on the physicochemical properties of natural rubber.

3. RESULTS AND DISCUSSION

The physicochemical properties of the raw rubber samples subjected to phenol-based oxidative discoloration were determined. The results of the analyzed parameters which include dirt content, volatile matter, initial plasticity (Po), plasticity at 30 minutes (P_{30}), plasticity retention index (PRI), ash content, and nitrogen content are shown in Table 1.

Table 1: Physicochemical Properties of Raw Rubber Samples (Mean ± SD, n = 3)

Pallet No.	Dirt (%)	Volatile Matter (%)	P_0	P_{30}	PRI	Ash (%)	Nitrogen (%)
401	0.04 ± 0.01	0.67 ± 0.02	55 ± 1.00	43 ± 1.00	78 ± 1.53	0.22 ± 0.01	0.23 ± 0.01
403	0.02 ± 0.01	0.63 ± 0.01	56 ± 0.58	46 ± 1.15	82 ± 1.00	0.22 ± 0.01	0.24 ± 0.01
404 (Ctrl)	0.03 ± 0.01	0.60 ± 0.02	51 ± 1.53	47 ± 0.58	82 ± 0.58	0.24 ± 0.01	0.22 ± 0.01

Values are expressed as mean ± standard deviation (n = 3).

4. DISCUSSIONS

4.1 Dirt Content

The dirt content of the raw rubber samples is presented in Table 1, while the graphical representation is shown in Figure 4. The values obtained ranged from 0.02–0.04%, with pallet 401 recording the highest dirt content (0.04%), pallet 403 the lowest

(0.02%), and the control sample, pallet 404, having an intermediate value of 0.03%.

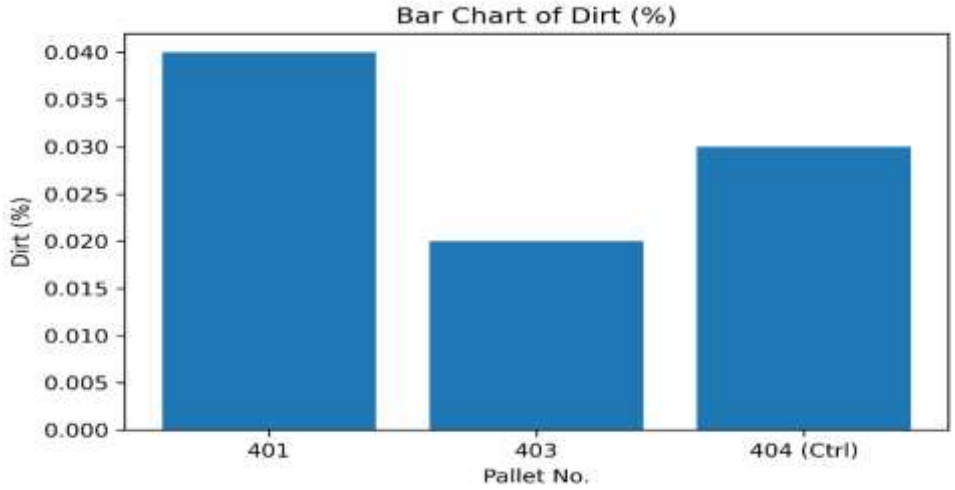


Fig. 4: Bar chat of dirt content

The observed differences in dirt content may be associated with variations in handling conditions, coagulation processes, and contamination during latex collection and processing. Dirt content is an important quality parameter in natural rubber because excessive impurities can adversely affect processing efficiency, mechanical performance, and product appearance (Akinlabi and Ogunniyi, 2021). The slightly higher value recorded for sample 401 may indicate greater exposure to environmental contaminants such as bark particles, soil debris, and coagulated non-rubber residues during tapping or drying. However, all samples, including the oxidatively discolored samples and the control (404), remained well below the maximum allowable limit of 0.05% specified for technically specified rubber grades under ISO 247 standards. This indicates that phenol-based oxidative discoloration had minimal influence on the accumulation of insoluble impurities within the rubber matrix. Similar findings were reported by Zhang *et al.* (2022), who observed that oxidative browning reactions in natural rubber primarily affect colour formation and oxidative stability rather than significantly altering dirt content.

The control sample (404) exhibited slightly lower contamination compared with sample 401, suggesting that the absence of pronounced oxidative discoloration may have contributed to better surface cleanliness and reduced retention of oxidized particulate matter. Nevertheless, the generally low dirt values obtained confirm that all rubber samples maintained acceptable industrial quality with respect to impurity content.

4.2 Volatile Matter

The volatile matter content of the rubber samples is presented in Table 1, while the graphical illustration is shown in Figure 5. The values obtained ranged from 0.60–0.67%, with sample 401 recording the highest value (0.67%) and the control sample, 404, showing the lowest (0.60%).

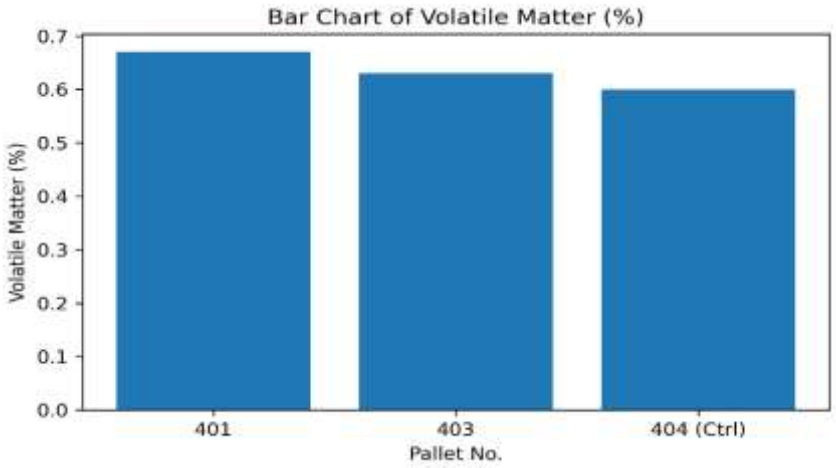


Fig. 5: Bar chat of volatile matter

The slightly elevated volatile matter observed in samples 401 and 403 may be attributed to residual moisture and low-molecular-weight volatile substances retained during processing. Increased volatile matter can promote oxidative reactions and accelerate phenolic discoloration during storage and thermal exposure. The control sample (404) exhibited lower volatile content, indicating better drying efficiency and improved storage stability.

Nevertheless, all samples remained below the maximum permissible limit of 0.80% specified for technically specified natural rubber, confirming acceptable processing quality. The results suggest that phenol-based oxidative discoloration may contribute slightly to moisture retention and oxidative susceptibility but did not significantly compromise the overall quality of the rubber samples.

4.3 Initial Plasticity (P_0), Plasticity after Ageing (P_{30}), and Plasticity Retention Index (PRI)

The values of initial plasticity (P_0), plasticity after thermal ageing (P_{30}), and plasticity retention index (PRI) for the rubber samples are presented in Table 1, while their comparative graphical representation is shown in Figure 6.

The P_0 values ranged from 51–56, indicating that all samples possessed good molecular integrity and acceptable processing characteristics. Sample 403 recorded the highest P_0 value (56), while the control sample (404) showed the lowest (51). Following accelerated ageing, P_{30} values ranged between 43–47, with sample 401 exhibiting the greatest reduction, suggesting higher susceptibility to oxidative degradation.

Similarly, PRI values varied from 78–82%, with samples 403 and the control (404) recording the highest oxidative stability. The comparatively lower PRI value observed in sample 401 indicates that phenol-based oxidative discoloration may have slightly reduced resistance to thermal oxidation through chain scission and degradation of the rubber matrix.

However, all samples maintained PRI values above the minimum industrial requirement of 60%, confirming that the rubber samples retained acceptable quality and ageing resistance despite the occurrence of oxidative discoloration.

4.4 Ash and Nitrogen Content

The ash and nitrogen contents of the raw rubber samples are presented in Table 1,

*Corresponding author, e-mail: iyobosa.iyawe@uniben.edu, praiseapo2021@gmail.com
https://doi.org/10.60787/FJSIR.v10i1.109-119
©Scientific Information, Documentation and Publishing Office at FUPRE Journal

while their combined graphical representation is shown in Figure X.

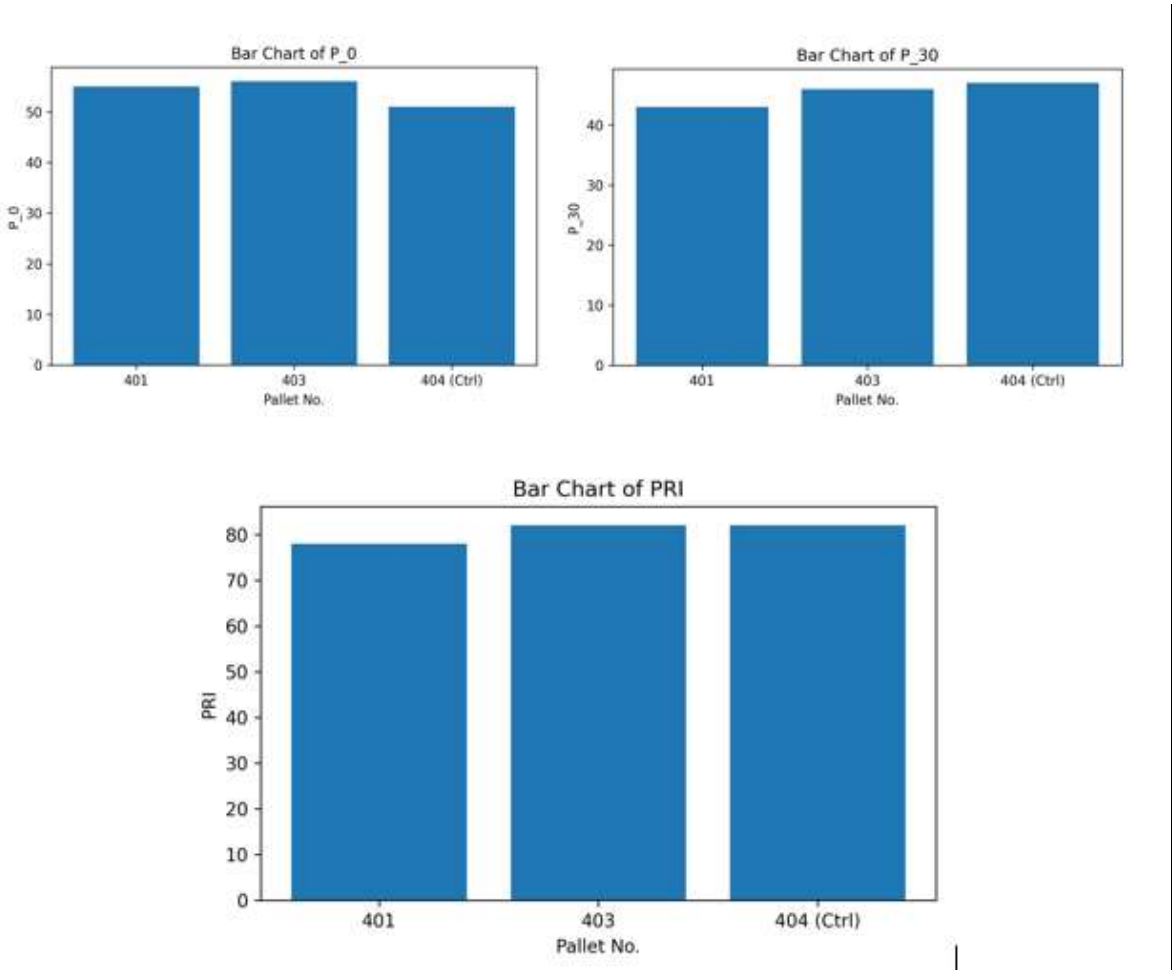


Fig. 6: Bar chat of Initial Plasticity (P_0), Plasticity after Ageing (P_{30}), and Plasticity Retention Index (PRI)

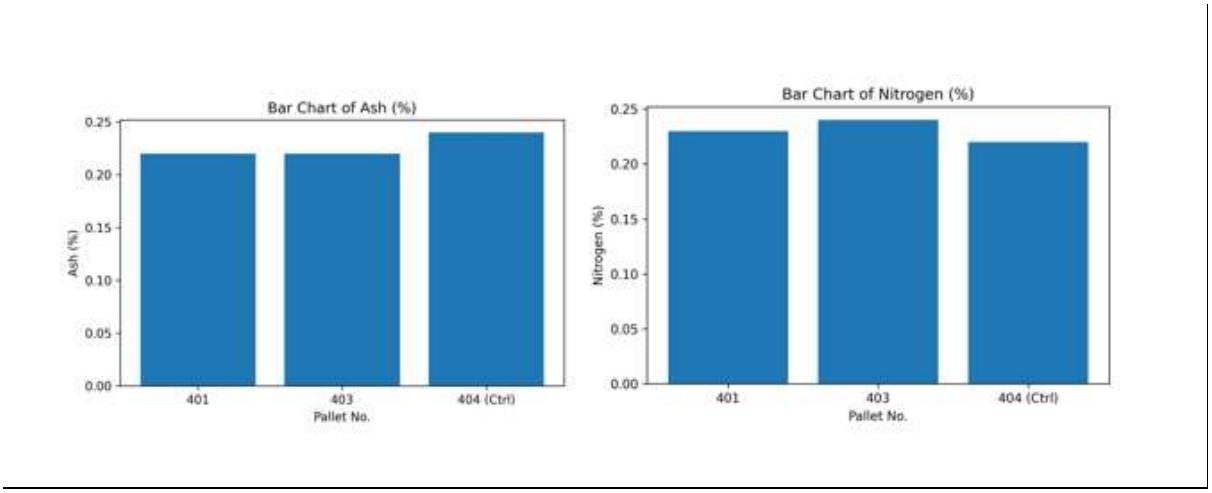


Figure 7: bar chat of Ash and Nitrogen Content

The ash content ranged from 0.22–0.24%, with the control sample (404) recording the highest value. These low ash values indicate minimal inorganic contamination and confirm that all samples complied with acceptable industrial standards for technically specified rubber. The slight increase observed in the control sample may be attributed to minor residual mineral constituents retained during processing.

Nitrogen content values ranged between 0.22–0.24%, with sample 403 showing the highest value and the control sample the lowest. Nitrogen in natural rubber is mainly associated with proteins and other non-rubber constituents, which can influence oxidative reactions and colour stability. The slightly higher nitrogen content observed in the oxidatively discolored samples suggests that protein–phenolic interactions may have contributed to the discoloration process.

Overall, the results indicate that phenol-based oxidative discoloration had minimal effect on the inorganic composition of the rubber samples, although slight variations in nitrogen content may influence oxidative behaviour and long-term storage stability.

5 CONCLUSION

This study investigated the effect of phenol-based oxidative discoloration on selected physicochemical properties of natural rubber obtained from Hevea brasiliensis latex. The evaluated parameters included dirt content, volatile matter, ash content, nitrogen content, initial plasticity (P_0), plasticity after ageing (P_{30}), and plasticity retention index (PRI). The results showed that oxidative discoloration had only slight influence on the measured properties of the rubber samples. Samples affected by discoloration exhibited marginal increases in volatile matter and nitrogen content, alongside slight reductions in P_{30} and PRI values, indicating a moderate effect on oxidative stability and thermal ageing resistance. However, dirt and ash contents remained low and within acceptable industrial limits, suggesting that discoloration did not significantly increase impurity levels or inorganic contamination. Among the samples analyzed, pallet 401 showed comparatively lower oxidative stability, as reflected by its reduced PRI value and higher volatile matter content, whereas the control sample (404) maintained better overall stability. Nevertheless, all samples satisfied the standard requirements for technically specified natural rubber, confirming that the observed phenol-based discoloration did not critically compromise rubber quality. Overall, the findings demonstrate that oxidative discoloration in natural rubber is primarily associated with minor physicochemical changes related to phenolic oxidation and protein interactions rather than severe deterioration of material quality. This study therefore provides useful insight into the relationship between phenolic discoloration and raw rubber properties, contributing to improved quality assessment and processing control in natural rubber production.

Acknowledgments

The authors express their sincere gratitude to the department of chemistry, University of Benin, Nigeria,

REFERENCES

Akinlabi, E.T. and Ogunniyi, D.S. (2021). Quality assessment of technically specified natural rubber and the influence of processing contaminants. *Journal of Rubber Science and Technology*, 94(3), 215–223.

AOAC (2016) *Official Methods of Analysis of AOAC International*. 20th edn. Gaithersburg, MD: AOAC International.

*Corresponding author, e-mail: iyobosa.iyawe@uniben.edu, praiseapo2021@gmail.com

https://doi.org/10.60787/FJSIR.v10i1.109-119

©Scientific Information, Documentation and Publishing Office at FUPRE Journal

ASTM (2013) *ASTM D1278 – Standard Test Method for Rubber from Natural Sources: Determination of Volatile Matter*. West Conshohocken, PA: ASTM International.

Bokobza, L. (2019). Natural rubber: Sustainable raw material for innovative applications. *Journal of Macromolecular Science, Part C: Polymer Reviews*, 59(2), 107–134.

Chen, Y., Liang, M. and Zhang, H. (2021). Effect of moisture and storage conditions on oxidative stability of natural rubber. *Polymer Degradation and Stability*, 188, 1–10.

Choo, K.T., Ismail, H. and Kamaruddin, A.N. (2019). Influence of oxidative ageing on the plasticity and mechanical properties of natural rubber. *Journal of Rubber Research*, 22(3), 145–154.

ISO (2017) *ISO 248-1: Rubber, raw — Determination of volatile-matter content — Part 1: Hot-mill method and oven method*. Geneva: International Organization for Standardization.

ISO (2020) *ISO 2007: Rubber, unvulcanized — Determination of plasticity — Rapid-plastimeter method*. Geneva: International Organization for Standardization.

ISO 247:2006. *Rubber — Determination of ash content*. Geneva: International Organization for Standardization.

ISO 247:2006. *Rubber — Determination of ash content*. Geneva: International Organization for Standardization.

ISO 248-1:2011. *Rubber — Determination of volatile matter content — Part 1: Hot-mill method and oven method*. Geneva: International Organization for Standardization.

ISO 2930:2019. *Rubber, raw natural — Determination of plasticity retention index (PRI)*. Geneva: International Organization for Standardization.

Karunarathne, W. (2018). Phenolic oxidation and enzymatic browning in natural rubber latex. *International Journal of Polymer Science*, 1–8.

Krishnan, A., Thomas, K.U. and George, S.C. (2019). Economic importance and global production trends of natural rubber. *Journal of Plantation Crops*, 47(2), 65–74.

Lv, M., Zhao, Y., Wang, X. and Liu, J. (2022). Mechanisms of oxidative discoloration in natural rubber and associated physicochemical changes. *Polymer Testing*, 110, 107562.

Mingzhe, L., Chen, Z. and Huang, Y. (2022) 'Color stability and quality evaluation of light-coloured natural rubber', *Journal of Applied Polymer Science*, 139(18), 51984.

Omar, M.F., Rahman, N.A. and Salleh, M.S. (2024). Natural rubber production and processing from Hevea brasiliensis: A review. *Materials Today: Proceedings*, 80, 2150–2158.

Rojruthai, P., Sakdapipanich, J. and Tanaka, Y. (2021). Role of non-rubber constituents in natural rubber discoloration and degradation. *Journal of Rubber Research*, 24(1), 55–67.

Siriwong, C., Nakason, C. and Kaesaman, A. (2015). Influence of non-rubber components on colour development in natural rubber. *Advanced*

Materials Research, 1125, pp. 247–252.

Surani, S. and Sagari, M. (2021). Polyphenol oxidase activity and enzymatic browning in natural rubber latex. *Industrial Crops and Products*, 171, 113936.

Wang, H., Li, Y. and Zhou, X. (2023). Industrial applications and performance enhancement of natural rubber materials. *Materials Chemistry and Physics*, 302, 127756.

Zhang, Y., Liu, H. and Chen, X. (2022). Effect of oxidative browning on physicochemical properties of natural rubber. *Polymer Testing*, 108, 107503.