Characterization of Semi-Processed Rubber (Hevea *brasiliensis* Willd.) Treated With Different Coagulants

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ABSTRACT

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A study was conducted to characterize the semi-processed rubber treated with different coagulants and to determine the relationship of physical and chemical properties of semi-processed rubber as treated with different coagulants.The different coagulants significantly influenced the characteristics of coagula such as pH reading of acid solution, pH reading of coagula, rate of coagulation, fresh weight and % DRC recovery. The different coagulants also significantly influenced the physical properties of semi-processed rubber such as Initial Plasticity(Po), Plasticity Retention Index, Color Index, Mooney Viscosity and % Dirt Content. The different coagulants did not significantly influence the chemical properties of semi-processed rubber such as % Nitrogen Content and % Volatile Matter, but significantly influenced the % Ash Content. No significant correlation between physical properties of semi-processed rubber such as Initial Plasticity(Po), Plasticity Retention Index, Color Index, and % Dirt Content and chemical properties of semi-processed rubber such as % Nitrogen Content and % Volatile Matter, but color index is positively correlated with % ash content of semi-processed rubber.

Keywords: rubber, latex, coagula, semi-processed rubber, physical properties and chemical properties.

Rationale: In the Philippines most of the natural rubber products that directly obtained from the producers are cup lumps with approximately 70% of the Philippines' total natural rubber production (PRDP, 2012). The remainder is processed into Technically Specified Rubber (TSR) (or crumb) and crepe rubber, usually in locations in the Zamboanga Peninsula, SOCCSKSARGEN and other major production hubs (Field Research, 2016). Moreover, the price of cup lump product depends on the quality and dry rubber content (DRC) taking into account the weight, volume and density. Some farmers and tappers thought that they are cheated by the traders every time they sell their product and in response they try to add foreign materials and substances to increase the weight, volume and density for greater sale, hence, a need to enhance accountability and establish traceability system. In the bigger sense, low class and inconsistent quality of semi-processed rubber and cup lumps makes it difficult for the industry to penetrate bigger and more lucrative markets. The occurrence of contaminants is hardly detectable through technical specification testing or even through visual inspection, especially when the rubber has been pressed to make a bale. The occurrence of impurities can cause considerable difficulties to the purchaser if not detected in the first steps of processing. The Philippines' rubber is believed to be substandard by industry actors. Domestic stakeholders said rubber used to be mixed with battery solution, dirt and other contaminants during initial processing (DA-Region XII, 2015). The quantity of field latex is lower and quality is inferior due to premature and in appropriate tapping methods and the practice of mixing other substances. In the preparation of wet coagulum, some tappers add contaminants intentionally such as sand and bark shavings and other foreign materials to increase weight. Others utilized battery solution as coagulating agent which is much low-priced than the suggested coagulant

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(formic acid). Others use coagulants recognized for the high water retention properties (Phuc, 2006). Standard grade rubber is coagulated with the used Formic and Acetic acid material. These acids are preferred on account of their volatile nature and being noncorrosive to the equipment used and acceptable quality of processed rubber. There are potential acid source available locality and the inappropriate used of this coagulating agent may hamper the superiority of process rubber and may double the cost in initial processing activities, hence, this study was conducted.

Objectives of the Study

The study was conducted to characterize the coagula and semi-processed rubber treated with different coagulants and to correlate the physical and chemical properties of semi-processed rubber. Specifically, the objectives of the study were the following:

1. to determine the characteristics of rubber coagula such as pH reading, rate of coagulation, fresh weight of coagula, and dried weight rubber crepe as treated with different coagulants;

2. to characterize the semi- processed rubber based on its physical properties such as the plasticity retention index (PRI/Po),color, dirt content, and viscosity and the chemical properties such as the nitrogen content, ash content and volatile matter as treated with different coagulants; and

3. to determine the relationship of the physical properties of semi-processed rubber, and the chemical properties of semi-processed as treated with different coagulants;

Significance of the Study

The paper was come up with the information on the characterization of the semi-processed rubber coagulated with different coagulants and that was correlated to the physical and chemical properties of the semi-processed rubber. The result of this study will serve as the guide for the rubber enthusiast and policy maker with the concern of rubber quality enhancements. This work will offer opportunity to the rubber farmers for the useful and efficient usage of potential rubber coagulants available in the locality and for the new researchers as basis for upcoming studies.

Assumptions of the Study

In this work, it was assumed that the rubber latex was collected and coagulated with different acids used in coagulation, and it was also assumed that the acid application was followed on the general recommendation for acid application of commercial grade coagulants and for the oxalic acid, battery solution and coconut vinegar as efficient coagulants. It was also assumed that the rubber latex that was coagulated come from "Clone RRIM 600" to avoid discrepancies upon the analysis as the different rubber clones have its peculiar attributes in its NR.

Scope and Delimitation of the Study

The study was limited to the characterization of the semi-processed rubber treated with different coagulants and to correlate the chemical and physical properties of semi-processed natural rubber as influenced by acid coagulant treatment.

Duration and Place of the Study

The collection of rubber latex and rubber milling was done in Testado Farm at Upper Pres. Roxas, North Cotabato. The Philippine Rubber Testing Center at the University of Southern Mindanao (PRTC) catered the laboratory analysis of the samples. This study was conducted from November 2018 to February 2019

REVIEW OF RELATED LITERATURE

Rubber Standardization

While regularly talk about to as a homogeneous item, the NR market is enveloped of an amount of various item types, which shift in handling strategies and have diverse end employments. There are three primary item groups: Latex concentrate and pale crepe, TSR and RSS, representing around 40, 38 and 22 percent of the market correspondingly (Accenture, 2014). Latex concentrate is fundamentally utilized in the assembling of therapeutic and buyer items, for example, medical gloves, contraceptives and teats, and so forth. TSR and RSS produces are typically used in the transportation, industrial, and clothing divisions. TSR is routinely named crumps (Field Research, 2016). Certain use of these items joint on the evaluation of rubber, which is constrained by elastic thickness perusing, levels contaminants and rate nitrogen focus, among others.

Constraints in Rubber Quality

Low quality latex creates low end class of blocks, for example SVR10. Likewise, the preparing of low quality raw latex involves an any longer (twofold) handling time, therefore longer utilization of hardware, and higher costs for power, water, work and strikingly, ecological expense for processing waste disposal (DA-Region XII, 2015). Latex may likewise be coagulated utilizing acids or organic product juice which isn't exceptional among smallholders who can't convey the latex to a handling task before it coagulates. The nature of these latex coagula (some of the time alluded to as 'smallholders latex' contrasts fairly from 'cup lumps', that is, latex which has been left to coagulate without anyone else in the tapper's container and in this manner has less contaminants (Field Research, 2016).

Properties of Natural Rubber

Rubber particles generally comprise of 93 to 95% poly (cis-1,4-isoprene,) (Surya *et al*., 2018) center encompassed by a perplexing membrane made of phospholipids (Sansatsadeekul et al., 2011; Reis et al., 2015). They evaluated the irregular close pressing of the suspension at Φrcp =0.715 (Shewan and Stokes, 2015). The association of proteins and phospholipids on the layer of these particles is as yet vague. A few creators have suggested that it is composed in patches (Nawamawat et al., 2011) while others accepted an auxiliary association in stratified layers (Rochette et al., 2013), with a thickness in the scope of 10 to 20 nm (Singh et al., 2003; Gaboriaud et al., 2012). Subsequent to tapping, distinctive biochemical responses in the NRL suspension result in its coagulation (Wititsuwannakul et al., 2008).

Hypothesis

The study hypothesized that the different coagulants do not significantly affect the characteristics of coagula, and the different coagulants do not significantly affect the physical and chemical properties of semi-processed rubber.

The study hypothesized also that the physical properties of semi-processed rubber do not significantly influence the chemical properties of semi-processed rubber treated with different coagulants.

METHODOLOGY

Experimental Design and Treatments

This study was carried out using a Completely Randomized Design (CRD) with five treatments and four replications. The different sources of acid materials served as the treatment of the study. The treatments were the following:

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A- 2% Coconut Vinegar

D- 2%Oxalic powder

B- 2% Formic Acid

F- 1% Battery Solution

C- 2% Glacial Acetic Acid

Preparation of Acid Coagulant

The commercial acid coagulant was prepared using its recommendations in dilution and those local materials possible source of acid. The concentrated acid coagulants were diluted in clean tap water to avoid any contamination of the future coagula. For coconut vinegar, it was undergone laboratory test to determine its concentration.

Harvesting of Latex and Acid Application

Natural rubber latex was extracted in already productive and mature rubber tress. The accumulated latex was collected and will proceed initial processing to remove any contaminants fresh harvested latex. The 500 ml of fresh latex was coagulated in plastic container and 500 ml of prepared acid solution was mixed to the fresh latex and will be allowed to coagulate until all the samples will coagulate completely.

Rubber Coagula Processing

The sample of rubber coagula treated with different coagulants was processed in Testado Village level rubber processing plant of located at Upper Pres. Roxas, North Cotabao. Coagula was processed 2 days after acid application and converted into sheets following village level processing schemes. The coagulum was passed through a pair of groove-surfaced rollers. To form the coagulum into thin sheets (2.5 mm), several passes at least 5 times was recommended. For each pass the clearance between the rollers was adjusted until a desired thickness of 2.5 mm was attained. During milling, clean water was applied to remove the serum, acids, and other impurities. The milled sheets was soaked in clean water in a tub, then these were hanged in horizontal bars placed in the dripping area to drip off water for about four hours in a shaded open air. The sheets were dried in a smoke house and were placed in the hangers provided above the slated flooring. Firing the dryer was done with the use of firewood. Temperature was maintained at 50 - 60^0C on the first and second day the. Drying time was about 3- 4 days. The dried sheets were folded and wrapped with polyethene bags. The sheets were labelled accordingly to its treatment. Samples were taken about 650 g for physical and chemical analysis.

Data Gathered

The data gathered in the experimental set-up were made up of characteristics of coagula, physical and chemical properties of rubber as treated with different coagulants. The physical properties were the initial plasticity (Po/PRI), dirt content, color, and viscosity. The Chemical properties were the nitrogen content, volatile matter and ash content.

Data Gathering

1. ***Characteristics of cagula***- The characteristics of coagula were determine through pH reading of coagula, rate of coagulation, fresh weight of coagula, and dried weight of rubber sheets.

a. **pH reading.**
b. **Rate of coagulation.**
c. **Weight of coagula**.
d. **Dried weights of the rubber sheets.**

Homogenization and Sequence of Preparations for Further Tests

The preparation of test piece was done following standard procedure adopting ISO 1796: 1982 (E) to homogenize the sample for various tests. The sample was passed through the roll mill having guides spaced of 200 to 280 mm apart. The length of the rolls was 300 mm and outside diameter was 150 $\pm$ 5 mm. The clearance between the rolls was adjustable from 0.2 – 3 mm and the speed of the slow roll was 24$\pm$ 1 rev/min. The ration ratio of the fast and slow roll was 1.4:1 rev/min and the hollow roll was for easy heating by steam and for cooling by running water. The calibration of mixer was done by heating the rolls at the temperature of 70$\pm$ 5^{0}C.

2. Physical properties of semi-processed rubber

Initial Plasticity (Po) / PRI. A standard procedure; Plasticity was adopted for initial plasticity (Po) of natural rubber and the plasticity retention index (PRI) as described by ISO 2930:2000(E)was The result was recommended (P_{30}). The PRI was calculated using the expression:

PRI= (P_{30}/P_o) 100

Where:

Po – is the initial of un-aged test piece

P_{30} – is the plasticity of the aged test piece sample after aging for 30 minutes at 140^{0}C.

Color Index. The color of raw rubber was compared and matched as closely as possible with that of standard colored glasses. The basis of calibration was the 'lovibond color scale' in amber units. The appropriate disc was the:

- No. 4/19A 1 - 5 units at 0.5 unit interval; and
- No. 4/19B 5 - 16 units at 1.0 unit interval.

Mooney Viscosity. The standard procedure adopting ISO 289-1; 2014 (E) was used to determine the Mooney Viscosity.

Dirt Content. Using ISO 249:2014 (E) dirt content was

3. Chemical properties of semi-processed rubber

a. ***Volatile matter.*** ISO 248: 2015 (E) was used to determine the volatile matter content of semi-processed rubber.
b. ***Nitrogen.*** The standard procedure adopting ISO 1656; 2014 (E) was used for determination of nitrogen content of the semi-proceed rubber.
c. ***Ash content.*** The ash content of the natural rubber was determined through standard procedure adopting ISO 247:2001(E).

Other Observations and Documentation

Possible other information was recorded and documentation of the postharvest handling of the rubber coagula was given emphasize in this study.

Statistical Data Analysis

The gathered was analyzed using Pairwise analysis particularly LSD Test to determine the significant differences among treatment and Correlation Analysis using Pearson's Correlation to determine the relationships of different variables of the study.

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RESULTS AND DISCUSSION

pH Reading of the Acid Solution

The characteristic of coagula in terms of pH reading of acid solution used as coagulant for rubber is presented in Table 1, Column 2. The analysis of variance (ANOVA) reveals that there is high significant differences (Fcom= 68.45**; Pr=0.000) among treatment means.

Among the acid coagulant used, the highest pH reading was observed at 2 % oxalic acid with the mean of 6.38, followed by 2% coconut vinegar with the mean pH reading of 6.0, 2% Glacial acetic acid with mean pH reading of 5.0, but comparable to 1% Battery solution with the mean of 4.75. The lowest pH reading was observed at 2% Formic acid with mean pH reading of 4.25, and respectively.

The above result implies that the different acid solution in an assigned concentration has differed in its level of acidity expressed as pH and the acid solutions with low pH reading indicates the strong level acidity and it were observed in 1% battery solution and 2% formic acid.

pH Reading of Coagula

The pH reading of coagula as treated with different coagulants is presented in Table 1, Column 3.The analysis reveals that there is high significant differences, (Fcom=6.36**; Pr= 0.0034) among treatment means.

Table 1. Characteristic of coagula in terms of pH reading of acid solution, pH reading of coagula, and rate of coagula as treated with different coagulants.

Coagulants	pH Reading of Acid Solution1/	pH Reading of coagula	Rate of Coagulation (hrs)
2 % Coconut vinegar	6.00^{b}	6.35^{a}	1.04^{d}
2 % Formic acid	4.25^{d}	5.75^{bc}	3.02^{a}
2 % Glacial acetic acid	5.00^{c}	5.25^{c}	1.05^{d}
2 % Oxalic acid	6.38^{a}	5.85^{ab}	2.48^{b}
1 % Battery solution	4.75^{c}	5.25^{c}	2.10^{c}
CV (%)	4.06	6.43	1

1/ - Means in the same column followed by common letter superscripts are not significantly different at 5% level Least (Significant Difference (LSD).

Table 2. Characteristic of coagula in terms fresh weight of coagula, oven dry weight of rubber, and dry rubber content recovery as treated with different coagulants.

Coagulants	Fresh Weight of Coagula1/	Oven Dried Weight of Rubber (kg) ns	Dry Rubber Content recovery (%)1/
2 % Coconut vinegar	2.75^{a}	0.95	34.83^{b}
2 % Formic acid	2.20^{c}	0.925	42.05^{a}
2 % Glacial acetic acid	2.20^{c}	0.9	41.48^{a}
2 % Oxalic acid (powder)	2.50^{b}	0.95	38.00^{ab}
1 % Battery solution	2.20^{c}	0.9	40.91^{a}
CV (%)	5.9	6.08	7.58

1/ - Means in the same column followed by common letter superscripts are not significantly different at 5% level Least (Significant Difference (LSD).

Among the coagulant used, 2% coconut vinegar have the highest mean pH reading of 6.35, but comparable to the result of the rubber treated with 2% oxalic acid as coagulants with the mean pH reading of 5.85. Followed by the results of the rubber treated with 2% Formic acid as coagulant with the pH reading of 5.75, but comparable to the results of the rubber treated with 2% oxalic acid.

The lowest pH reading of rubber coagula are observed at the rubber treated with 1% Battery solution and 2% Glacial acetic acid with the same mean pH reading of 5.25, but comparable to the results of rubber treated with 2% Formic acid, and respectively.

The result implies that the different acid solution treated as coagulant has different effect to the level of acidity of coagula in terms of pH reading. The rubber treated with 1% Battery solution and 2% Glacial Acetic acid contributes to the acidification of rubber during coagulation process. Normal coagulation is carried out by acidifying latex from approximately neutral (pH of about 7), to pH 5.4 (Intapun, 2010).In addition, Lu et al. (2006) states that the attraction between particles can be induced by a change in the physical-chemical composition such as a change in ionic strength or pH. The electrophoretic mobility of the rubber particles as a function of pH showed that the membrane of particles was negatively charged under storage conditions (pH 8.5, ionic strength =7 mM), and that this membrane charge decreased continuously with the pH decrease, as observed in previous studies (Sansatsadeekul *et al.*,2011).

Rate of Coagulation

Table 1, Column 4, and Figure 2 present the rate of coagulation of rubber treated with different coagulants. The statistical analysis reveals that thereis high significant differences (Fcom=8139.74**; P=0.000)among treatment means of rate of coagulation express as the number of hours after acid application. The longest duration of coagulant is observed in the rubber treated with 2% Formic acid with the mean of 3.02 hours, followed by the rubber treated with 2% Oxalic acid with the mean of 2.48 hours coagulation, Battery solution with the mean of 2.10 hours, and respectively. The shorter rate of coagulation was observed at the rubber treated with coconut vinegar with the mean of 1.04 hours after acid application, but comparable to the results of the rubber treated with Glacial acetic acid with the mean of 1.05 hours after acid application.

The above result implies that the fastest rate of coagulation was observed in 2% coconut vinegar and 2% Glacial acetic acid. The stronger the acidity levels of the coagulants solution, the longer the rate of coagulation.Hernandez *et al.* (2006) demonstrated the function of pH on rubber because pH could change the interactions among colloidal particles. In addition, Sansatsadeekul *et al.* (2011) reported that the electrophoretic mobility of the rubber particles as a function of pH, isoelectric pH of 3.18 (pHi) corresponding to zero mobility.

Fresh Weight of Coagula

Table 2, Column 2 presents the fresh weight of coagula treated with different coagulants. The analysis of variance reveals that high significant differences was observed (Fcom= 13.18**, Pr=0.0001) among means of Fresh weight of coagula. The highest Fresh weight was significant observed in coagula treated with 2% coconut vinegar with mean weight of 2.75 kg. The least with the same mean weight of 2.20 kg were observed at coagula treated with 2% Formic acid, 2% Glacial acetic acid and 1% Battery solution, respectively.

The above results implies that the different coagulants significantly influenced the fresh weight of coagula and it shows that coconut vinegar accumulates more moisture in its pre-milling stage.

Oven Dried Weight of Rubber Sheets

The oven dried weight of rubber sheets treated with different coagulants is presented in Table 2, Column 3.Analysis of variance reveals that the different treatment of coagula did not significantly influence the oven dried weight of coagula. Only numerical differences were noted among treatment means which the weight of dried rubber sheets as treated with different coagulants, the means ranged 0.925, 0.950 kg, and respectively.

The result implies that the different coagulants did not influence the dried weight of rubber sheets, and the accumulation of dried rubber content was further relates to other parameters.

Dry Rubber Content Recovery

The Table 2, Column 4 presents the % Dry Rubber Recovery of the rubber treated with different coagulants. The analysis results reveals that the treatment of different coagulants significantly influence (Fcom=4.07*; Pr=0.098) the % Dry Rubber Content recovery.

The highest Dry Rubber Content recovery was observed atthe rubber treated with 2% Formic Acid with the Dry Rubber Recovery mean of 42.05, but the statistically comparable to the rubber treated with 2% Glacial acetic acid with the mean of 41.48%, 1% Battery Solution with the mean of 40.91 %, 2% oxalic acid with mean of 38.0%, respectively. The least was observed at the rubber treated with 2% coconut vinegar with the mean of 34.83%, but comparable the results treated with 2% oxalic acid.

The above result implies that the different coagulants treated significantly influenced the percentage (%) Dry Rubber Content recovery of Semi-Processed Rubber. Since the price of rubber greatly relies on the rubber quality and DRC(DA-Region XII, 2015) and to obtain higher returns, DRC of rubber must be considered upon using types of coagulants. On the other hand, DRC is also the physiological response which considered as a strong indication of bio-synthetic activity of lactiferous vessels of the rubber tree (Manero et al; 2003; Monero et al; 2007; Giraldo-Vasquez and Velasquez-Restrepo, 2017).

Physical Properties of Semi-Processed Rubber

Initial Plasticity (Po)

The physical properties of Semi-Processed Rubber interms of Initial Plasticity (Po) is presented in Table 3, Column 2.The statistical analysis reveals that there were high significant differences (Fcom= 52.50**; Pr= 0.0000) among treatment mean of Initial Plasticity of Semi-Processed Rubber.

The rubber treated with 1% Battery Solution as coagulants have the highest Initial Plasticity with the mean of 43.5, followed by the rubber treated with 2% Glacial acetic acid with Initial Plasticity mean of 35.25. However the least was observed at the rubber treated with 2% Oxalic acid with plasticity mean of 31.75, but the statistical comparable to the results of the rubber treated with 2% formic acid with the mean of 32.50, and 2% coconut vinegar with the Initial Plasticity mean of 33.25, respectively.

The results presented above lead into the implication that the different coagulants significantly influenced the Physical properties of Semi-Processed rubber in terms of Initial Plasticity. Moreover, the initial plasticity of the rubber is treated with different coagulants in this study passes the specification schemes of the Philippine Tested Rubber as attested by the Philippine Rubber Testing Center at USM. Based on the sub-graded of the PTR, plasticity of rubber within the minimum value of 30 and the value of Po of the study ranged from 31.75 to 43. Initial plasticity is the ability of rubber to deform (Prasertsit et al., 2011).High original and aged plasticity values usually correspond to good aging properties (Dick, 2003).

Plasticity Retention Index

Table 3, Column 3presents the physical properties of Semi-processed rubber in terms of Plasticity Retention Index of Rubber as treated with different coagulants. The result reveals that there were high significant difference (Fcom= 47.61**; Pr=0.000) among treatment means.

The highest Plasticity Retention Index was observed in the rubber treated with 2% Oxalic acid with the mean of 97.25. It is followed by the rubber treated with 1% Battery solution with the mean of 86.75, but comparable to the results of rubber treated with 2% Glacial Acetic Acid with the mean of 85.75. The least was observed at the rubber treated with 2% coconut vinegar with the mean 0f 70.25, but comparable to the result of the rubber treated with 2% Formic acid with the mean of 73.25 PRI value.

The above result implies that the used of 2% Oxalic acid to coagulated rubber significantly enhance the Plasticity Retention Index of the Semi-Processed Rubber as compared to the standard and commercially available glacial and acetic acid. However, based on the Philippine Tested Rubber (PTR) specification scheme, the PRI limits for Rubber Grade acceptability is minimum PRI value of 60 and the PIR results of this study passes the limits for Rubber Grades.The PRI is an indicator of raw rubber susceptibility to thermo-oxidative breakdown (Intapun, 2010)a measure of a rubber's thermal stability and aging resistance which can be directly related to the cleanliness of the rubber (Akrochem n.d), and classify quality and processability at factory level of natural rubber (Dick et al., 1999; Kundo, 2014). The higher the PRI, the higher the resistance of rubber to thermal oxidation breakdown which reflect the quality of the semi-processed rubber.

Color Index

Table 3, Column 4 presents the physical properties of rubber in terms of Color Index Calibrated using Loviband scale 2000. The analysis result reveals that there were high significant differences (Fcom= 15.23**; P= 0.000)among treatment means.

The highest color intensity was observed at the rubber treated with Oxalic acid with the mean color index of 5.0, but comparable to the results of rubber treated with 1% Battery Solution and 2% coconut vinegar with the same mean of 4.5, followed by the rubber treated with 2% formic acid with the mean color index of 3.5, and the lightest color intensity was observed in rubber treated with 2% Glacial acetic and was coagulant with the mean color index of 2.7.

The above results implies that the different coagulant used in Rubber coagulation is significantly influence the color index of semi-processed rubber

Table 3. Physical properties of semi-processed rubber in terms of initial plasticity (Po), plasticity retention index, and color Index as treated with different coagulants

Coagulants	Initial Plasticity (Po)[1/]	Plasticity Retention Index[1/]	Color Index (Lovibond 2000)[1/]
2 % Coconut vinegar	33.250[c]	70.250[c]	4.500[a]
2 % Formic acid	32.500[c]	73.250[c]	3.500[b]
2 % Glacial acetic acid	35.250[b]	85.750[b]	2.750[c]
2 % Oxalic acid (powder)	31.750[c]	97.250 [a]	5.000[a]
1 % Battery solution	43.500[a]	86.750[b]	4.500[a]
CV (%)	3.75	3.85	11.49

[1/]- Means in the same column followed by common letter superscripts are not significantly different at 5% levelLeast (Significant Difference (LSD)).

and the rubber treated with 2% glacial acetic acid and rubber treated with 2% oxalic acid, and 2% coconut vinegar produces the lightest color of rubber sheets as express in amber units using lovibond scale. Color play significant role because in some instances manufacturers prefer lighter color rubber particularly for fashion items like shoes and other foot wares , as Dick (2003) emphasizes that darker rubber may require additional amounts of TiO2 to meet a brightness standard and reflects additional cost in manufacturing processes.

Mooney Viscosity

The physical properties of semi-processed rubber was treated with different coagulant is presented in Table 4, Column 2. The analysis results reveals that there were high significant differences (Fcom=167.39** Pr=0.0000) were observed among treatment means the highest viscosity was observed at rubber treated with 15 battery solution with the viscosity mean of 70.00, followed by rubber treated with 25 Glacial acetic acid with the mean viscosity of 59.13, 2% coconut vinegar with the mean viscosity of 57.50. The least was observed at the rubber treated with 2% Oxalic acid with the mean Viscosity of 54.5.

The result implies that the different coagulants significant influenced the Mooney viscosity of semi-processed rubber and the highest viscosity is observed in 1% battery solution and rubber treated with this kind of coagulants harder semi-processed product. Mooney viscosity is commonly used to characterize and monitor the quality of both natural and synthetic rubber. It measures the resistance to flow of the rubber at a relatively low shear rate (Dick, 2003).

Table 4. Physical properties of semi-processed rubber in terms of Mooney Viscosity and Percent Dirt Content treated with different coagulants

Coagulants	Mooney Viscosity % Wt. ML (1+4) 100 degree C1/	% Dirt Content 1/
2 % Coconut vinegar	57.500[c]	0.0075[bc]
2 % Formic acid	56.250[c]	0.0042[c]
2 % Glacial acetic acid	59.125[b]	0.0100[b]
2 % Oxalic acid (powder)	54.500[d]	0.0163[a]
1 % Battery solution	70.000[a]	0.0155[a]
CV (%)	1.59	25.71

1/- Means in the same column followed by common letter superscripts are not significantly different at 5% level (Least Significant Difference (LSD).

Percentage Dirt Content

The physical properties of semi-processed rubber in terms of percentage dirt content of as treated with different coagulants are presented in Table 4, Column 3. The analysis of variance reveals that there were significant differences among treatment means.

The highest dirt content was observed in rubber treated with 2% Oxalic acid with the mean dirt content of 0.0163 %, but comparable to the results of rubber treated with 1% Battery solution with the mean dirt content of 0.0155%, followed by rubber treated with Glacial acetic acid with the mean dirt of content of 0.01%. The least was observed in rubber treated with 2% Formic acid with the mean dirt content of 0.0042%, but comparable to the results of rubber treated with 2 % coconut vinegar with the mean dirt content of 0.0075%.

The above result implies that the different coagulants used significantly influence the accumulation of dirt in processing semi-processed rubber. However, the semi-processed rubber produced from the coagulation of different coagulants passed the Philippine Tested Rubber (PTR) Specification. Scheme limits for rubber grades which the dirt content of within the maximum of value of 0.02% and the dirt content semi-processed samples of the study is relatively lower from the limits. Moreover, According to Giroh et al. (2006),quality of rubber produce depends on the purity of the latex/coagula obtained from the rubber trees. The presence of any form of foreign body in them can adversely affect the quality of the end product which offered low price for the coagula/latex. According to Dick (2003) impurities in natural rubber have a degrading effect if the rubber is a performance expected polymer. This is especially important for tire applications where small particles of dirt in critical places can cause tread separation. In connection to this, Akrochem (n.d.) states that premium grades rubber have visually lower dirt content and excellent properties and low dirt also results in high quality physical properties of natural rubber.

Chemical Properties of Semi-Processed Rubber

Nitrogen Content

The chemical properties of semi-processed in terms nitrogen content is presented in Table 5, Column 2. The analysis of variance reveals that there was no significant difference among treatment means. Only numerical differences were noted in which the mean of % nitrogen content ranged from 0.588, 0.593, 0.595, 0.698, 0.743, respectively.

The above result implies that the different coagulants did not significantly influence the accumulation of nitrogen of semi- processed rubber. Nitrogen is primarily from the accumulation of proteins and amino acids in dry rubber (Moreno et al., 2005).

Table 5. Chemical properties of semi-processed rubber in terms of Nitrogen content, Volatile matter, and Ash content treated with different coagulants.

	Nitrogen Content (% Wt.)ns	Volatile Matter (% Wt.)ns	Ash Content (% Wt.)[1/]
Coagulants			
2 % Coconut vinegar	0.595	0.718	0.4050[a]
2 % Formic acid	0.588	0.863	0.3825[ab]
2 % Glacial acetic acid	0.593	0.763	0.3400[b]
2 % Oxalic acid (powder)	0.698	0.74	0.3950[a]
1 % Battery solution	0.743	0.81	0.4025[a]
CV (%)	20.8	20.5	7.75

[1/] - Means in the same column followed by common letter superscripts are not significantly different at 5% level (Least Significant Difference (LSD).

Volatile Matter

Table 5, Column 3 presents the chemical properties of semi-processed rubber in terms of Volatile Matter as treated with different coagulants. The analysis of variance reveals that there is no significant difference among treatment means. Only numerical differences were noted among treatment means in which % nitrogen content of rubber treated with 2 % Coconut vinegar

(0.718), 2% Oxalic acid (0.740), 2% Glacial acetic acid (0.763), 1% Battery.

solution (0.810), 2% Formic acid (0.863), respectively

The result leads into implication that the different coagulants used did not significantly influenced the chemical properties of semi-processed rubberin terms of % volatile matter. PTR limits for rubber grades Specification scheme, rubber volatile matter is within the maximum range of 0.8% and the volatile matter in this study is relatively within the minimum range for acceptability for the rubber grades. The higher the volatile matter, the higher moisture content and other rubber hydro carbons of the rubber products (Dick, 2003).The high volatile matter in dry rubber is the negative implication in the quality of semi-processed rubber. Moisture in dry rubber may affect the development of fungal contamination in the store products. Appropriate drying can answer in dealing with moisture in semi-processed rubber.

Percent Ash Content

The chemical properties of semi-processed rubber in terms percent sh content as treated with different coagulants is presented in Table 5, Column 4. The statistical analysis reveals that there were significant different (Fcom= 3.19* ; Pr= 0.0440) among treatment means of ash content of semi-processed rubber as treated with different coagulants.

The highest percent (%) ash content is observed at rubber treated with 2% Coconut vinegar with the mean of 0.405, but comparable to the results of rubber treated with 1% Battery solution with the mean of 0.403, 2% Oxalic acid with the mean of 0.395, and also the rubber treated with 2% Formic acid with the mean of 383% nitrogen. The least was observed at the rubber treated with 2% Glacial acetic acid with the mean of 0.340, but comparable to the result of rubber treated with 2% Formic acid.

The above result implies that the different coagulants significantly influenced the percent of ash content of semi-processed rubber. The PTR limits for rubber grades ash content is within the minimum ranged of 0.6 in, the type of rubber in this study and the % ash content of rubber is relatively lower its limiting value. Ash content is considered important parameter in determining quality of rubber products. As Dick (2003) emphasized that percent ash is important because a high value can indicate a higher specific gravity and can ultimately affect curing characteristics of the rubber compound. The higher ash content the higher the impurities in processed rubber which ash in dry rubber suspected as fine mineral fillers, calcium carbonate, talc, aluminum silicate, and clay (Dick, 2003).

Relationship between Physical and Chemical Properties of Semi-processed Rubber Treated with Different Coagulants

The relationship between physical and chemical properties of semi-processed rubber treated with different coagulants is correlated using Pearson's product-moment correlation and presented in Table 6.

The Physical Properties of semi-processed rubber in terms of Initial Plasticity (Table 3, Figure 8) is not significantly correlated to the Nitrogen (r= 0.3320; P= 0.1527), Initial Plasticity is not significantly correlated to Volatile Matter (r= 0.0272; P= 0.9093), and Initial Plasticity is not significantly correlated to % of Ash Content (r= 0.0818; P= 0.7318). However, the Initial

Plasticity is positively correlated (r= 0.9811; P=0.0000) to other physical properties of semi-processed rubber which particularly the Mooney Viscosity. As the Initial Plasticity increases, the Mooney Viscosity is also increase significantly.

Plasticity Retention Index (Table 3, Figure 9) is not significantly correlated to Nitrogen Content (r=0.2631; P= 0.2624), not significantly correlated to Volatile Matter (r= 0.0499; P= 0.8346), and not significantly correlated to Ash Content (r= -0.1165; P= 0.6246). However, Plasticity Retention Index is significantly correlated (r= 0.7629**; P= 0.0001) to Dirt Content.

Color index (Table 3 and Figure 10) is not significantly correlated (r= 0.2941; r= 0.2082) to Nitrogen Content, not significantly correlated (r=0.0057; P= 0.9811) to Volatile Matter, and significantly correlated (r= 0.5883; P= 0.0064) to Ash Content. The Color index and Ash content is positively associated with each other. The higher the color intensity, the higher the % Ash content of semi-processed rubber.

Mooney Viscosity (Table 4 and Figure 11) is not significantly correlated (r= 0.2942; P= 0.2082) to Nitrogen, not significantly correlated (r= 0.0042; P= 0.9860) to Volatile Matter, not significantly correlated (r= 0.2942; P= 0.2082) to Dirt Content (Table 4 and Figure 12) is not significantly correlated (r= 0.3045; P= 0.1917) to Nitrogen, not significantly correlated (r= 0.1112; P= 0.6406) to Volatile Matter, and not significantly correlated (r= 0.1892; P= 0.4242) to Ash content of semi-processed rubber.

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Table 6. Pearson's product-moment correlation in relationship between physical and chemical properties of semi-processed rubber treated with different coagulants ((Prob > |r|)

Parameter	Statistic	Physical Properties					Chemical Properties		
		Initial Plasticity (P0)	Plasticity Retention Index (PRI)	Color Index	Mooney Viscosity	Dirt Content	Nitrogen Content	Volatile Matter	Ash
Initial Plasticity (P0)	Coef,r	1	0.1158	0.0093	0.9811	0.3747	0.332	0.0272	0.0818
	p-value		0.6269	0.9689	0.0000**	0.1036	0.1527	0.9093	0.7318
	n	20	20	20	20	20	20	20	20
Plasticity Retention Index	Coef,r	0.1158	1	0.2669	0.076	0.7629	0.2631	-0.0499	-0.1165
	p-value	0.6269		0.2553	0.7501	0.0001**	0.2624	0.8346	0.6246
(PRI)	n	20	20	20	20	20	20	20	20
Color Index	Coef,r	0.0093	0.2669	1	0.0326	0.4283	0.2941	0.0057	0.5883
	p-value	0.9689	0.2553		0.8914	0.0596	0.2082	0.9811	0.0064**
	n	20	20	20	20	20	20	20	20
Mooney Viscosity	Coef,r	0.0093	0.2669	0.0326	1	0.4283	0.2941	0.0042	0.1227
	p-value	0.9689	0.2553	0.8914		0.0596	0.2082	0.986	0.6063
	n	20	20	20	20	20	20	20	20
Dirt Content	Coef,r	0.3747	0.7629	0.4283	0.3305	1	0.3045	0.1112	0.1892
	p-value	0.1036	0.0001**	0.0596	0.1557		0.1917	0.6406	0.4242
	n	20	20	20	20	20	20	20	20

** - Highly Significant (P= <0.01 or 0.01)
* - Significant (P= >0.01 or 0.05)
ns - Not Significant (P= > 0.05)

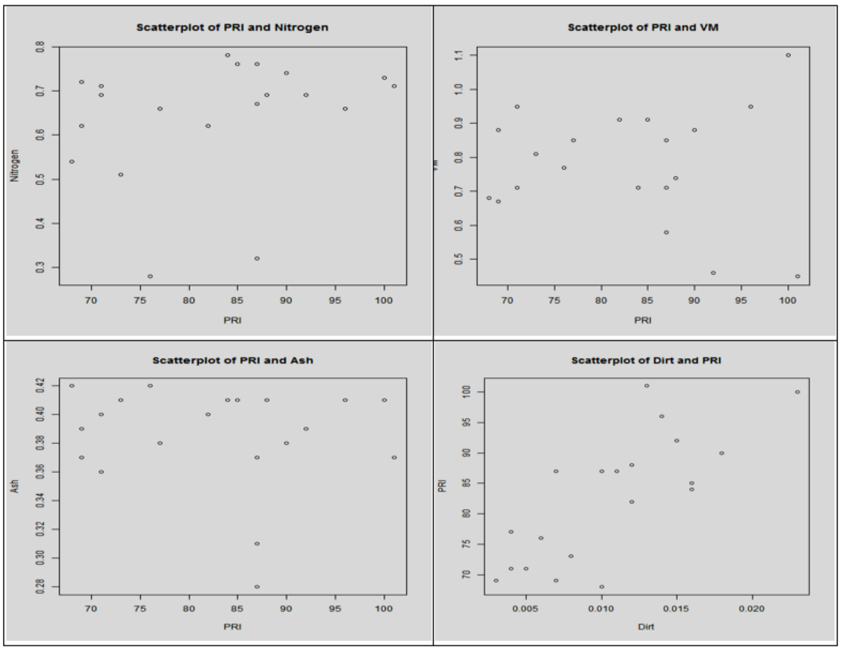

Figure 3. Scattered plot of the Plasticity Retention Index as correlated with Nitrogen, Volatile Matter, and Dirt Content treated with different coagulants.

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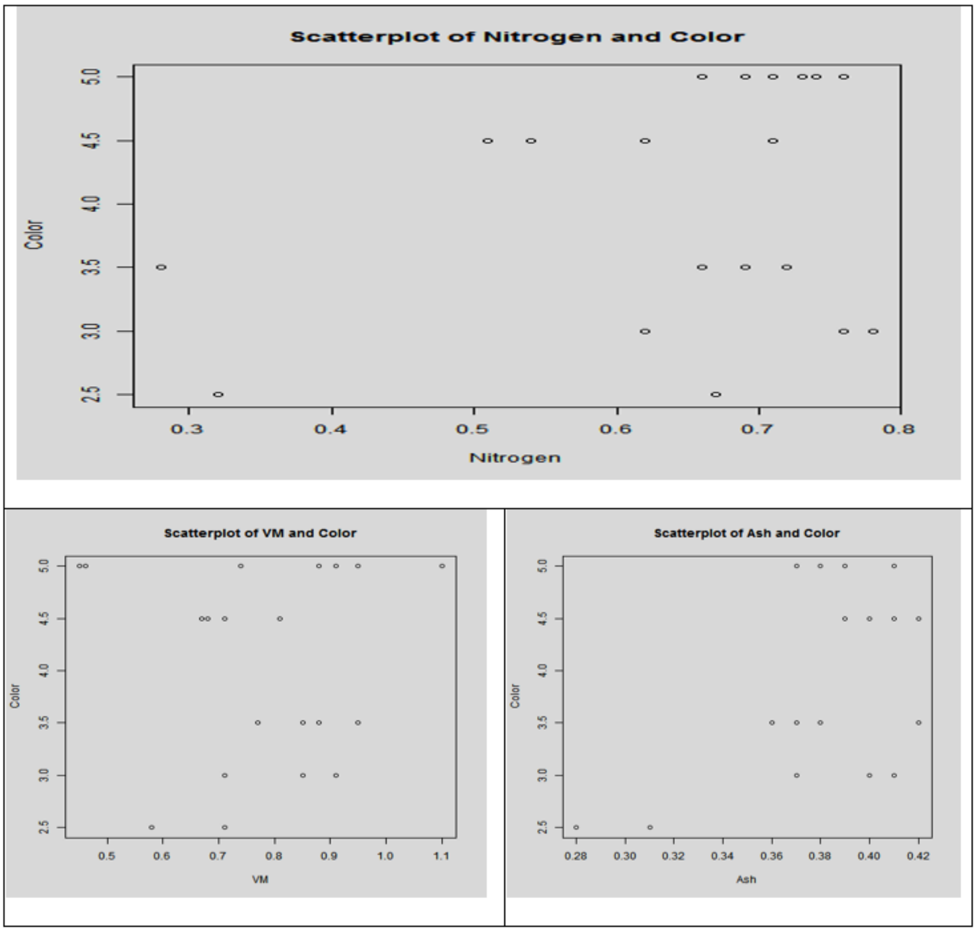

Figure 4. Scattered plot of the Color as correlated with Nitrogen, Volatile Matter, and Ash treated with different coagulants.

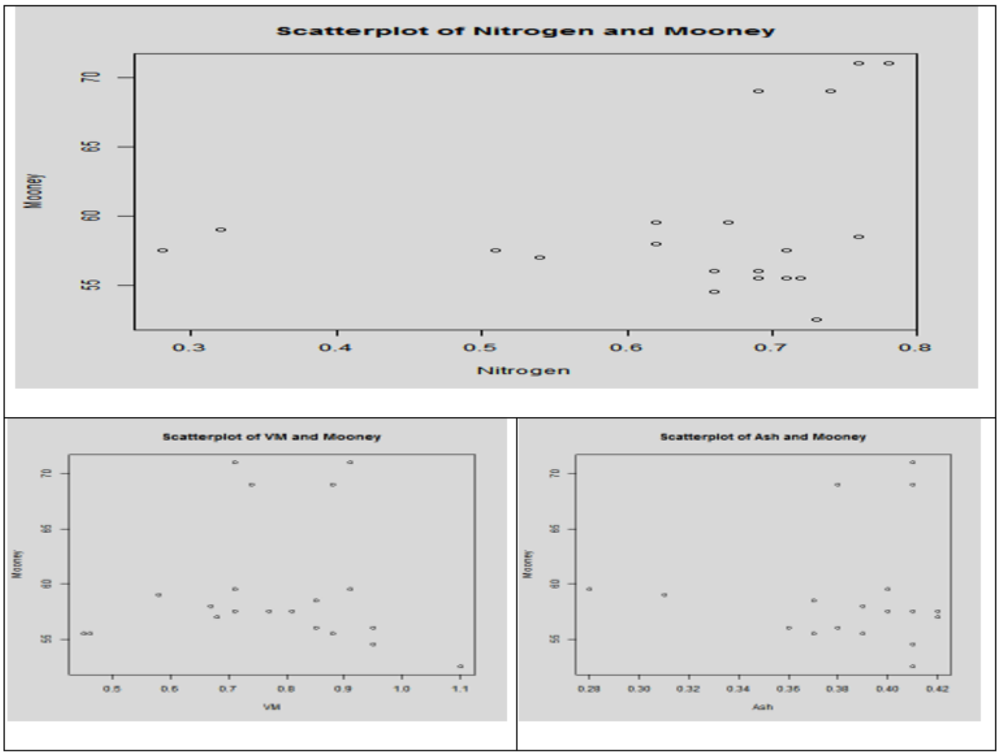

Figure 5. Scattered plot of the Color as correlated with Nitrogen, Volatile Matter, and Ash treated with different coagulants.

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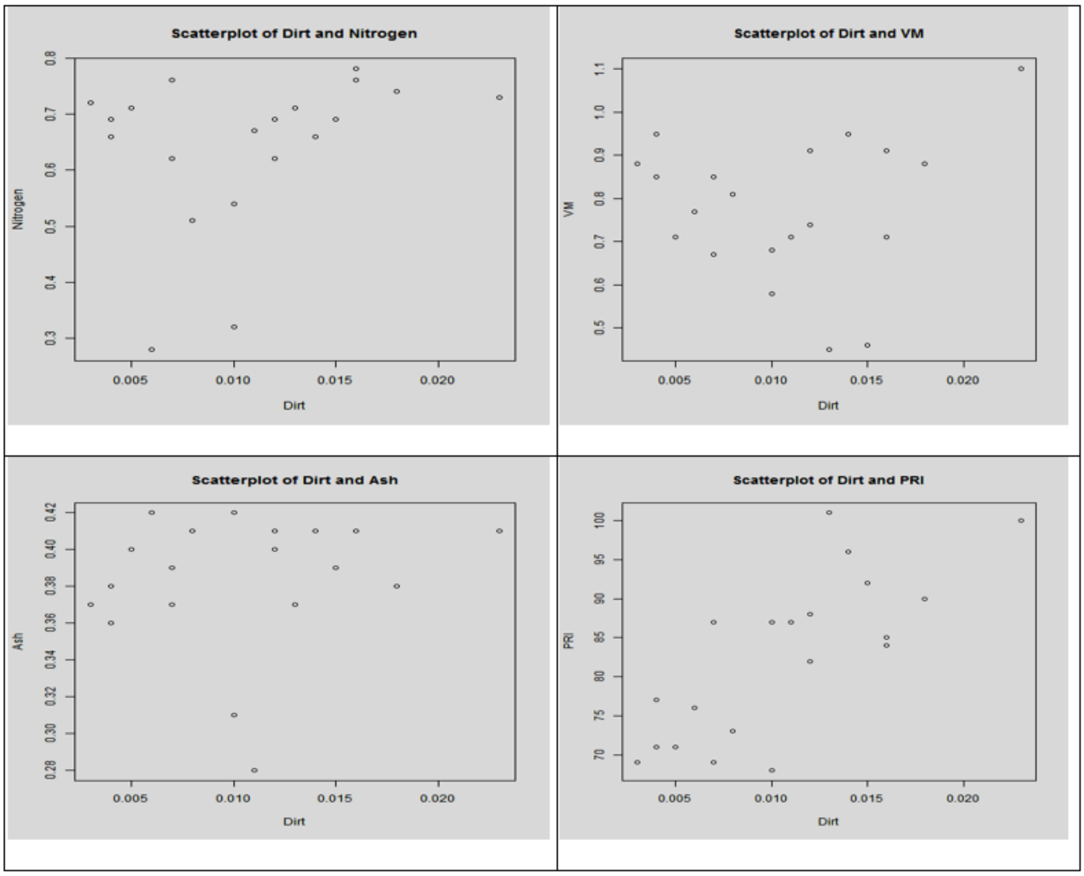

Figure 6. Scattered plot of the Dirt Content as correlated with Nitrogen, Volatile Matter, Ash, and Plasticity Retention Index as treated with different coagulants.

As observed during the use of different coagulants, the rubber coagulated with 1% battery solution showed discoloration on the coagula 24 hours after milling coagula and consequently produces darker semi-processed rubber (Figure 4). It was also observed that the rubber treated with 2% oxalic acid produced very soft coagula and when it was milled breakage of the rubber sheets was noticed (Figure 4). In milling, very soft coagula are not desirable for the reason of breakage and tarring-off of the rubber sheets during drying processes. However, in economic side and efficient use of different coagulants was also observed in which large amount of coconut vinegar is required to compensate the desirable concentration of its level of acidity and in the case of this study, equal quantity of coconut vinegar to the rubber latex was used. This large quantity of coconut vinegar is not considered as economical in the farmer's side considering the price Php 50.00/gallon.It was also observed in this study that there is irritation in the eyes and hands during the handling of coagula coagulated in this type of coagulants.

SUMMARY, CONCLUSION AND RECOMMENDATION

The following are the findings of the study:The different coagulants significantly influenced the characteristics of coagula such as pH reading of acid solution, pH reading of coagula, and fresh weight, and % dry rubber content (recovery),but did not significantly influenced the oven dried weight. The different coagulants significantly influenced the physical properties of semi-processed rubber such as Initial Plasticity (Po), Plasticity Retention Index (PRI), Color index, Mooney viscosity, and % Dirt content.The different coagulants significantly influence chemical properties of semi-processed rubber such as % ash content, but did not significantly influence the % nitrogen content, % volatile matter. The Physical properties of semi-processed rubber such as Initial Plasticity is not significantly correlated to the, Volatile Matter, and % of Ash Content. However, positively correlated to Mooney Viscosity. As the Initial Plasticity increases, the Mooney Viscosity is also increase. Plasticity Retention Index is not significantly correlated to % Nitrogen Content, Volatile Matter and Ash Content. However, Plasticity Retention Index is significantly correlated to

Dirt Content. Color index is not significantly correlated to % Nitrogen Content, Volatile Matter. But positively associated with % ash content. The higher the color intensity, the higher the % Ash content of semi-processed rubber. Mooney Viscosity is not significantly correlated to Nitrogen, Volatile Matter, and Ash Content. As been observed in this study, discoloration was observed in rubber sheets treated with battery solution and it produces darker color semi-processed rubber. Very soft coagula produced from oxalic acid.

Based on the results, it was concluded that the different coagulants significantly influenced the characteristic of coagula, enhances physical properties, and chemical properties of semi-processed rubber (% Ash). Color index is positively associated with % ash content of semi-processed rubber. The battery solutions produce hard coagula in pre-millings stage and the undesirable discoloration in post milling stage.

This study recommends that the locally available source of acid like coconut vinegar, oxalic acid is potential materials for rubber coagulation. Upon using the coconut vinegar as coagulant, this material must undergo laboratory analysis to determine the level of acidity and to obtain the appropriate concentration of the acid solution. Coconut vinegar can be used as coagulants for rubber with the concentration of 2 %. The oxalic acid is within the concentration of 2 % or 20 grams per litter of water is good rubber enhancers in terms of PRI and it is recommended that this material must further be explored to treat with poor quality raw rubber.

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APPENDICES

Appendix A. Analysis of variance of pH reading of acid solution					
Source of Variance	**df**	**Sum of Square**	**Mean Square**	**Fcom**	**Pr (> F)**
Coagulants	4	12.5500	3.1375	68.4500	0.0000**
Error	15	0.6875	0.0458		
Total	19	13.2375			

CV = 4.06%

Appendix B. Analysis of variance of pH reading of coagula coagulatreated with different coagulants.					
Source of Variance	**df**	**Sum of Square**	**Mean Square**	**F Value**	**Pr (> F)**
Coagulants	4	3.4080	0.8520	6.3600	0.0034**
Error	15	2.0100	0.1340		
Total	19	5.4180			

CV= 6.43%

Appendix C. Analysis of variance of rate of coagulation (hrs) treated with different coagulants.					
Source of Variance	**df**	**Sum of Square**	**Mean Square**	**F Value**	**Pr (> F)**
Coagulants	4	12.2639	3.0660	8139.74	0.0000**
Error	15	0.0057	0.0004		
Total	19	12.2695			

CV=1.00%

Appendix D. Analysis of variance of fresh weight of coagula as treated with different coagulants.					
Source of Variance	**df**	**Sum of Square**	**Mean Square**	**Fcom**	**Pr (> F)**
Coagulants	4	1.0280	0.2570	13.1800	0.0001**
Error	15	0.2925	0.0195		
Total	19	1.3205			

CV=5.90%