The Study of Liquid Smoke as Substitutions in Coagulating Latex to The Quality of Crumb Rubber

Saharman Gea1*, Nur Azizah1, Averroes F Piliang2, Hanifa Siregar1

1Department of Chemistry, Faculty of Mathematics and Natural Science, Jalan Bioteknologi No.1, Kampus Universitas Sumatera Utara, Medan, 20155, Indonesia
2Department of Physics, Faculty of Mathematics and Natural Science, Jalan Bioteknologi No.1, Kampus Universitas Sumatera Utara, Medan, 20155, Indonesia

Corresponding Email: s.gea@usu.ac.id

Abstract. The use of formic acid in processing rubber is considered unaffordable in large-scale plantations. However, the demands of this acid are increasing as the number of rubber plantations increases higher. In addition to solve this challenge, the use of liquid smoke has been considered promising substitutes although its most suitable composition has not been estimated yet. To understand the effect of liquid smoke as coagulant material in rubber industries, a research is conducted by mixing of the coagulant material (combination of liquid smoke synthesized from coconut shell and formic acid) onto latex. Characterizations are performed to analyse the quality of the coagulated rubber, and they are the initial plasticity, the plasticity Retention Index, the dirt content, the ash content, the content of dry rubber. The result showed that the formulation of liquid smoke and formic acid give effect to produce crumb rubber and quality rubber appropriate of Standard Indonesian Rubber (SIR) 20.

Keywords: formic acid, liquid smoke, coagulant, latex, Rubber Indonesian Standard

1. Introduction

According to the quality standard issued by Indonesia National Standard (SNI 06-2047-2002), the coagulant suggested for natural rubber is formic acid. This suggestion is based on its relatively safe characteristics. Another coagulant that has been used widely is acetate acid, however this acid could damage the quality of rubber. More importantly, the use of chemical compounds must be focusing on its function in coagulating without damaging the quality of the crumb rubbers.

As it is mentioned previously, formic acid is effective in coagulating because of its safety. However, the cost of using formic acid is considerably expensive in the scale of plantation. To reduce the cost, many chemicals have been used such as sulphuric acid [1] and smoke acid [2]. Therefore, many attempts have been performed to use certain alternatives. For instance, Indonesian farmers have used Triple Super Phosphate (TSP) fertilizers, pineapple essence which are not considered to use[3]. Nevertheless, the coagulating agents must be safe, and affordable.

The process of rubber coagulation actually is affected by its acidity. The adding of acidic compounds could reduce the value of pH to isoelectric points which can cause losing of charge within the rubbers. Therefore, chemical compounds which will be used must able to maintain the charge within the rubber particles. Another important factor that must be observed is the cleanliness of the rubber, which is antifungal.
Given that liquid smoke has antioxidant characteristics, this material could be used as an alternative. It has been reported that liquid smoke was able to prevent the growth of microorganisms [4], and insects [5]. This ability as antimicrobial is based on the presence of phenolic compounds within the liquid. The compositions of chemicals have been accounted for phenols (4.13%), carbonyl (11.3%), and acid (10.2%) [6]. The degree of pH of liquid smoke is appropriate in coagulating the rubber which is around 1.76 – 2.97 [7]. Therefore, this study aims to investigate the effect of liquid smoke in coagulating process based on standard quality of crumb rubber issued by SNI.

2. Experimental
2.1 Materials
Latex was supplied by local plantations at Simpang Empat, sub-district Sei Rampah, Serdang Bedagai Regency, Sumatera Utara Province. Formic acid (94%) was supplied by PT Sintas Kurama Perdana, while the liquid smoke was afforded from Coco Production House in third grade. In addition to prepare the samples, mineral turpentine and Curio TsSol (36%) were purchased from PT Batanghari Tebing Pratama.

2.1.1 Preparation Coagulation Process by Formic Acid and Liquid Smoke
As many as three liters of latex was prepared, and it is divided into 6 vessels for 100 mL which is based on Suwardin and Purbaya[8]. Then, 30 mL of 4% formic acid was prepared for one liter of latex, while the liquid smoke was prepared for 10% v/v of 100 mL of latex. The percentage of combination of formic acid (FA) and liquid smoke (LS) is shown on Table 1 below.

| Label | Percentages (%) FA/LS | Volume (mL) FA/LS |
|-------|------------------------|-------------------|
| A     | 100/0                  | 3/0               |
| B     | 80/20                  | 2.4/2             |
| C     | 60/40                  | 1.8/4             |
| D     | 40/60                  | 1.2/6             |
| E     | 20/80                  | 0.6/8             |

Every vessels added with the coagulating agents was stirred until the samples coagulated while at the same time, the time of coagulation was measured by stopwatch. After being coagulated, each of coagulated rubbers was ground for six times with creeper-instruments. Then, the samples were dried for 10 days under direct sunlight followed by 100°C inside an oven. Next, the samples were grounded for three times to be prepared for plasticity tests, viscosity, and purity of dried rubber.

2.2 Characterizations
2.2.1. Characterization of Plasticity
The dried samples were prepared, and as many as 15 g of dried samples was grounded for three times. Then the rubber sheet was folded in half, pressed slowly with the palm of the hand. After being pressed, the samples of rubber sheet were cut with Wallace punch tools as many as six pieces of test with 13 mm of diameter respectively. Initial plasticity and after removal was measured.

2.2.2. Measurement of Mooney Viscosity
The viscosity tool is heated for 1 hour. Each sheet of rubber sample was taken 2 pieces of test with the Wallace Punch tool. Put the rotor into the first rubber sample that has been given a hole with scissors. The second example is placed on top of the rotor and then put together into the lower rotor. The top stator is closed and after being closed the stopwatch is turned on. After exactly one minute, the rotor is run. The viscosity value is read with a pointing device. The number shown by the micrometer needle after the fourth minute is the value of rubber viscosity.
2.2.3. Determination of Ash Content
Clumped latex weighed as much as 5 g of samples which had been uniformed, then cut into pieces and put in a porcelain cup which was first dried and weighed. The sample is heated to reach the temperature in Muffle Furnace (550°C) for 2 hours until it is not blurred again. Platinum platter is cooled in the desiccator to room temperature, and then weighed.

2.2.4. Determination of Dirt Levels
Weighed the sample as much as 10 grams, then put it into Erlenmeyer which was filled with mineral turpentine as much as 230 mL and Curio Ts Sol 36% as much as 1.2 mL, then heated in an infrared box with a temperature of 255°C for 2 hours and during heating it was shaken several times until dissolved well, beforehand the filter was weighed empty and the filter number was recorded, then after 2 hours then the solution was filtered, then rinsed Erlenmeyer with washing bottle to clean the dirt that remained at the bottom of Erlenmeyer, then dried the filter in an oven for 1 hour until it reached room temperature, then the filter and the coolant are cooled, then weighed and weighed the filter containing dirt.

2.2.5. Determination of Dry Rubber Content
Latex was weighed to determine the latex weight, then dried rubber ± 25 times with a thickness of 6.9 mm to clean the samples from contaminants such as pieces of rubber skin, moss, leaves, sand and so on, then rolled the mill, then weighed again to determine the rubber weight dry.

3. Results and Discussion
3.1 Time Coagulation

Table 2. Time coagulation of each samples based on the percentages

| Label | Percentages (%) FA/LS | Time |
|-------|-----------------------|------|
| A     | 100/0                 | 6’46”|
| B     | 80/20                 | 8’1” |
| C     | 60/40                 | 10’11”|
| D     | 40/60                 | 12’15”|
| E     | 20/80                 | 14’26”|

The latex clumping process is affected by changes in the rubber particle load in the latex, so that the interaction power of the rubber with its protector becomes lost. Rubber particles that are free will combine to form clots.

It can be seen in the table above that the substitution of liquid smoke for formic acid affects the speed of the latex clumping process. The fastest coagulation process was obtained by coagulant of formic acid without substitution of liquid smoke for 6 minutes 46 seconds, while the longest coagulation was obtained on liquid smoke substitution by 20%. This happens because the concentration of 4% formic acid has a higher effectiveness to reduce the latex pH to reach the isoelectric point. However, this condition may change if the concentration of liquid smoke is more concentrated, or the concentration of formic acid is more dilute. The desired condition is that the latex can reach the isoelectric point at pH 4.5 - 4.8.

The speed of latex clumping is affected by pH. The conditions that are expected to get a short clumping time, are influenced by the coagulant concentration in order to accelerate the achievement of the isoelectric point. According to Manday (2008) the isoelectric point in latex is 4.5 to 4.8 (depending on the type of clone). In this study, the effort taken was to find the right concentration to be able to produce a good quality coagulum, but with a faster clotting time compared to other alternative coagulants. The coagulation is displayed by following Figure 1.
Based on Figure 1, the colour produced by A as coagulating agent showed darker colour than it is produced by E. The darker patterns gradually decreased until E sample which was coagulated by higher use of liquid smoke for 80%/20%.

3.2 Rubber Quality of Plasticity

The magnitude of the effect of substitution of liquid smoke on formic acid as a latex coagulant material on the value of the initial plasticity of rubber processing material can be to meet SIR 20 seen in the following Figure 2.

According Figure 2 above, the highest initial plasticity value is the sample treated with 100% formic acid. Overall the plasticity value of all these treatments has met the criteria of SNI 1903-2011 with a minimum value of initial plasticity is 30.

The change in initial plasticity seen in the results of this study is influenced by the addition of liquid smoke. This happens because the effectiveness of antioxidants owned by liquid smoke is weakened due to the concentration of phenol contained in liquid smoke, and it decreases due to dilution of the coagulant to a concentration of 10%. So, it is unable to protect the polymer chain from...
oxidation reactions. The value of plasticity decreases until the combination of (60:40) % formic acid and liquid smoke, then it returns to an increase in the ratio of (40:60) % formic acid and liquid smoke.

![Figure 3. Index Retention of Plasticity](image)

From Figure 3 above it can be seen that the highest value was obtained with 100% formic acid is 82%, while the lowest PRI value is obtained in liquid smoke substitution 40% by 36%. The retention index values show rubber resistance to oxidation degradation. If the value is low, it shows that rubber is easily oxidized or vice versa. In this study, it can be seen the influence of liquid smoke as a formic acid substituent, that the addition of liquid smoke further decreases the plasticity value of rubber index retention.

According to Fessenden and Fessenden[9] formic acid is the strongest compounds from carboxylic acid groups and it functions as a reducing agent. Whereas according to Luditama[7] identified components of liquid smoke from coconut shell with pyrolysis temperature of 300°C using GC-MS analysis obtained 26 compounds with dominant phenol compounds (34.45%), 2,6-dimethoxy phenol (12.58%) and 2-methoxy phenol (9.81%).

Based on the data above, it can be seen that the two coagulant materials are antioxidants, which can protect rubber particles from degradation due to oxidation. However, the antioxidant properties of liquid smoke are not as strong as formic acid as the strongest acid. Thus, the concentration of liquid smoke 10% has not been able to reach the 4% formic acid antioxidant power.

3.3 Mooney Viscosity
To understand the characteristics of viscosity, the samples were tested by performing the Mooney viscosity. The following graph which is Figure 4 shows the viscosity of each samples, treated with combination of formic acid and liquid smoke.
Based on Figure 4 above, it can be seen that the values of Mooney viscosity from several formulas obtained shows interesting point. The use of 100% of formic acid had the same value 80%/20% of LS/FA. The minimum value obtained was in liquid smoke substitution for 40% at 71 and the highest Mooney viscosity value was liquid smoke substitution 20% at 78.

### 3.4 Ashes Content

From Figure 5 above obtained the maximum value of ash content obtained by 80% liquid smoke substitution of 0.30% (b / b) and the minimum value of ash content obtained by 100% formic acid by 0.19%. Nevertheless, overall all formulations used in this study have ash content values that meet SNI 1903: 2011.

In the above data it can be seen that the addition of liquid smoke as a formic acid substituent has a significant effect. Addition of liquid smoke increases the value of ash content. According to Kartowardoyo (1980) ash content is influenced by foreign material contamination factors and the type of coagulant material used. This increase in ash content is influenced by the addition of liquid smoke, this is because the minerals contained in this grade 3 liquid smoke accumulate during testing.
3.5 Dried Rubber Content

Based on the graph of Figure 6, the maximum dry rubber content accounted at 80% substitution of liquid smoke by 41.26% (w/w). This value exceeds the control value which is coagulant 100% formic acid. While the minimum dried rubber value was obtained in the formulation of 40% liquid smoke by 37.36% (w/w). The dry rubber content decreased due to the addition of liquid smoke as a substituent for formic acid. According to Kartowardoyo[10], heating that occurs in rubber causes the breaking of the rubber molecular chain. These rubber molecular chains will become free radicals because of the influence of air, such as oxygen, and this will bind to oxygen. The bonding of rubber molecular chains with oxygen causes the molecular chain of rubber to be short so that the molecular weight becomes smaller. This is related to the antioxidant strength of the coagulant given to the latex, as well as the antioxidant properties of the rubber particles themselves.

4. Conclusion
Based on the results of this study it can be concluded that the addition of coconut shell liquid smoke as a formic acid substituent gives an effect on the quality of the crumb rubber. The most significant changes influenced by the liquid smoke were high amount of dried rubber content which accounted for 41%, and the index plasticity retention for 47%. The others properties were almost similar to the rubber samples coagulated with formic acid. Overall, liquid smoke as substituents in latex coagulation affected the quality crumb rubber products which meet the Standard Indonesian Rubber (SIR) 20.

Acknowledgements
Acknowledgements are given to head laboratory of PT Batanghari TebingPratama for its permission in conducting this research, and the director of Coco Production House for their liquid smoke supplies.

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