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Impact of Latex Coagulant Various from Rubber Industry in South Sumatera

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Abstract: Rubber commodity is one of the superior commodities in South Sumatra. The main problem of the rubber industry that remains unsolved is that the product has a low quality due to poor handling of its raw material. Most farmers, in South Sumatera, often uses coagulant that are not recommended, namely sulfuric acid or para vinegar, alum, TSP fertilizer, a combination of para and alum vinegar, and others such as yam, and *tempe* washing water. Para vinegar, TSP fertilizer, alum and pineapple/ pineapple juice are acidic which cause smells of ammonia and sulfides. The liquid waste generated in the material process pollutes the environment if it is not properly intervened. Material handling in a rubber factory causes several illnesses for workers. However, the correlation of pollutants with these illnesses are not yet and become the focal point of this report.

Keywords: coagulant, environment, health, natural rubber

INTRODUCTION

Indonesia is the main producer and exporter of natural rubber after Thailand [1]. Rubber is one of the superior commodities in South Sumatra. Every year, rubber production increases in South Sumatra [1], [2]. There are 31 rubber factories in South Sumatra. Most of these natural rubber factories are in Palembang City [3]. Latex is produced from rubber trees [4]. Latex can be made into sheets and blocks of rubber [5]. Before natural rubber latex becomes rubber, it will become an elastic gel. The process is called coagulation [6]. Coagulation happens naturally or intentionally with the addition of coagulant [7], [8].

There are several coagulants that are often used, namely: Formic acid, Deurub K or liquid smoke, Sulfuric acid, Alum, Triple Super Phosphate (TSP) Fertilizer, Combination of para and alum Vinegar, Others such as yam, and *tempe* wash water [9]–[11]. Coagulation using citric acid and acetic acid requires a lot of water, is not environmentally friendly [12], and is dangerous for workers and the community [13].

Based on the background above, this paper will describe the types of coagulants, the mechanism of rubber coagulation and the impact of natural rubber processing.

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COAGULANT

There are two types of coagulants, as shown in Table 1:

TABLE 1. Types and number of coagulants used

Types of Coagulants	Total (%)
Recommended	
Formic acid	7
Deurub K or liquid smoke	1
Not recommended	
Sulfuric acid	66
Alum	10
Triple Super Phosphate (TSP) Fertilize	8
Combination of Sulfuric acid and alum	7
Others such as water of *Dioscorea hispida*, and *tempe* washing water	1

Source: [9], [10], [14]–[19].

Formic Acid

Formic acid [64-18-6] HCOOH, Mr 46.03, is a colorless liquid with a pungent odor, completely miscible with air and lots of polar solvent, and dissolved in hydrocarbons. Formic acid is a corrosive liquid that is colorless, clear and has a sharp odor. This substance is the strongest substituted alkyl carboxylic acid (pKa 3.74) [20]. Formic acid has been identified as a toxic intermediate (format) in methanol poisoning [21].

Formic acid, the simplest carboxylic acid, is found in nature or can be easily synthesized in a laboratory (a major by-product of several second-generation biorefinery processes), an important chemical because of its diverse application in the pharmaceutical and industrial fields [20], [22], [23]

Formic acid has been used to induce NAG coagulation [24]. Formic acid is the preferred choice for thickening latex, a suspension of microscopic natural rubber particles (polyisoprene) in aqueous media. The surface of the charged latex particles, which creates repulsion between them, prevents coagulation. In the coagulation process, formic acid neutralizes this charge, eliminating repulsion. This process produces consistent, high-quality natural rubber products. The use of strong acids makes the pH drop too fast and not homogeneous. As a result, latex clumps unevenly, which can affect its mechanical properties. Poor acids, such as acetic acid, are less efficient than formic acids and result in much higher consumption of acids [20].

Formic acid is one of the recommended coagulants. This formic acid produces good levels of dry rubber [14]. But this material cannot inhibit bacterial growth, so that it produces H_2S gas which causes a foul odor [14], [25].

Deurub K or Liquid Smoke

Liquid smoke is produced by the pyrolysis process of cellulose, hemicellulose, and lignin components [26]. The contents of liquid smoke compounds are phenolic compounds, aldehydes and ketones, furans and pyrans, organic acids, carbonyl compounds, and acetic acids [27]–[29]. Liquid smoke has antimicrobial, antioxidant effects, and organoleptic properties. This phenomenon is caused by the content in it to deactivate food spoilage organisms and foodborne pathogens [30]. One of the coagulants that produce good quality natural rubber is liquid smoke [31]. Liquid smoke is produced from a minimum of sawdust or wood chips. The use of different materials produces different levels of phenols, carbonyl, and organic acids as well [32].

Pure liquid smoke coagulants function as antibacterial, antioxidant, prevent odor, and environment friendly. This liquid smoke coagulant has a disadvantage that is a slow coagulation process. Coagulation is slow and requires more doses at a pH of a concentrated solution of around 2.5-3.0. Moreover, this coagulation has become less efficient [14].

Sulfuric Acid

Sulfuric acid is a strong (inorganic) mineral acid. This substance is soluble in water. This substance has many uses in various processes, namely solvents, reagents, acidic atmosphere, preservation, et Sulfuric acid has characteristics: liquid, clear, and odorless [33]. Acetic acid is known as vinegar (CH_3COOH) is a liquid, colorless,

pungent compound, has a sharp acidic taste, and dissolves in water, alcohol, glycerol, and ether. At atmospheric pressure, the boiling point is 118.1 °C [34]. According to Chemfinder (2006) & HSDB (2005), Sulfuric acid is very corrosive and has a sharp odor. Although not flammable, concentrated sulfuric acid mixed with water produces large amounts of heat [35], [36]. Sulfuric acid reacts strongly with organic materials, chlorates, carbides, fulminates, water, and powdered metals. When heated, sulfuric acid emits a highly toxic smoke in the form of sulfur trioxide. Sulfuric acid in the atmosphere that settles can reduce the pH of surface water and has a corrosive effect on living and non-living components [35]–[37].

Sulfuric acid (H_2SO_4) is a chemical compound classified as strong acid and corrosive to metals such as steel. Sulfuric acid harms the health of farmers and workers in the rubber industry. But material with sulfuric acid as a latex coagulant is still accepted by crumb rubber processing plants. The quality of the material still meets the SIR 20 type requirements [15].

Alum

Alum is a chemical with the formula $KAI(SO_4)_2 \cdot 12H_2O$. Aluminum is a hard, strong, small density, and resistant to corrosion. Alum production can be carried out by dissolving material containing Al_2O_3 in sulfuric acid solution. One source of Al_2O_3 in nature is found in kaolin soil. The reaction between kaolin and the sulfuric acid solution will produce an aluminum sulfuric solution. Solid alum is obtained from the crystallization process of saturated aluminum sulfate solutions [38]–[40]. Alum is called coagulant because it can cause coagulation. Coagulation is the process of coagulation through chemical reactions [41], [42]. According to Solichin et al., (2005) alum impacts rubber quality, including high ash content, low plasticity, and high water content [9].

TSP (Triple Super Phosphate)

Triple Super Phosphate is an artificial fertilizer in the form of granules (prill) made from the reaction of phosphate rocks with phosphoric acid. This process produces compounds with the main component of monocalcium phosphate $(H_2PO_4)_2$ [43]. Superphosphate is one type of fertilizer containing phosphorus (P) in the form of an oxide (P_2O_5) of 45%. TSP fertilizer is gray or light brown. Phosphorus (P) can be soluble in water and slightly acidic [44], [45].

According to Darussamin, Anwar & Yahya (1985) TSP fertilizers harm the material quality, including 1) dirt levels and ash levels increase; 2) the value of plasticity and the viscosity of Mooney and 3) the nature of rubber vulcanisate are low [9].

MECHANISM OF RUBBER COAGULATION

Coagulation is the event of a change in the sol phase into a gel phase which is aided by coagulant. Latex will be coagulum if the electric charge is lowered (dehydrated), the pH of the latex is reduced (addition of acid H^+), and the addition of electrolytes. The decrease in latex pH can be natural and the addition of coagulant [7], [8].

Schematic Rubber Particles

Latex is a colloidal dispersion system of poly (cis-1,4-isoprene) and $(C_5H_8)n$. Latex has ingredients, as shown in Table 2:

TABLE 2. Contents in latex rubber

Contents	Total (%)
Hydrocarbon chain	93,7
Natural lipids	2,4
Protein	2,2
Glycolipids and phospholipids	1,1
Carbohydrate	0,4
Inorganic material	0,2
Other compounds	0,1

Source: [46]–[48].

The rubber fraction contains rubber particles with a diameter of 0.05 - 3 µm. Rubber particles are cis hydrocarbon polymers 1.4 polyisoprene with molecular weights ranging from 400,000 - 1,000,000 [49]. This fraction is covered with a layer of protein and lipids. The function of this element is to stabilize the dispersion of rubber particles in the serum. The stability of the rubber particle dispersion is also caused by Brown's motion. The layer of water molecules that are firmly attached to the surface of the rubber particles. Rubber chains have a spiral shape that can heat like a spring, therefore rubber is rubbery (viscoelastic). The density of natural rubber is around 0.92 kg/m at 20 °C [18].

Coasservation / Destabilization

Coasservation /destabilization is a phenomenon of separation or phase change in a colloidal system. This process is called coagulation. Latex coagulation is a change in sol phase (latex) to gel phase (coagulum) [18], [50]–[53]. Latex will be coagulum spontaneously within a few hours of being collected. It is caused by 1) The activity of microorganisms decompose non-rubber materials so that acids arise in the rubber latex; 2) Fatty acids cause anions from the results of lipid hydrolysis that is in the latex. This anion will mostly react with magnesium and calcium ions. This process will form an undissolved soap and latex instability [18].

According to Gils and Suharto (1977) proved that during the storage of fresh latex, the fatty acids absorbed in the rubber phase increased. At that time, the concentration of magnesium ions in serum-C (serum centrifuge) increased too. These fatty acid ions and magnesium ions are the main causes of coagulum spontaneous. Coarservation or latex coagulation techniques can occur through (Barney, 1973): a) Addition of cations in the form of acid (H) or metal ions (M^{+}, M^{+2}, M^{+3}) such as Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Li^{+}, Na^{+}, and K^{+}; b) Addition of non-polar solvents; c) Adding hydrocarbon (oil emulsion) development materials [18].

Effect of pH on Latex Coagulation

The degree of acidity of fresh latex is 6.8 - 7. At this pH the latex is stable and will be not coagulum. The decrease and increase in pH will affect the latex [18], [54]. According to Abednego (1981) a decrease in pH can occur due to the formation of acids decomposed by bacteria in latex. Besides, the addition of coagulants can reduce pH to the isoelectric point. The coagulation also causes the rubber particles to lose their component so that the latex will be coagulum. The isoelectric point is a state of latex becoming unstable. This situation is called the area of critical stability potential at pH 3.7 - 5.5 [18].

Organic acids and inorganic salts occur in different mechanisms in coagulation. Coagulation with organic acids occurs in the mechanism of pH reduction. Coagulation with inorganic salts occurs because of the addition of salt cations as electrolytes. Latex stability is caused by the presence of a protein cover on the outside. The protein cover negatively contains. At a certain pH the positive contain the latex is balanced by the negative contain (an isolated point is reached). The addition of acid to the isolating point can disturb the stability of the latex, causing the coagulum. While the addition of electrolytes containing cations (the content is opposite to rubber particles) into the latex will cause a decrease in the electrokinetic potential so that it causes latex to coagulum [55].

Coagulation

Natural rubber latex is generally stabilized by the addition of a base such as ammonia or KOH. The negative charge transferred by cationic surfactants to the thin phospholipids, while the protein-membrane covers the rubber chain. Cationic stabilizers keep the macroscopic rubber particulate dispersion stable with electrostatic repulsion. Besides, these cationic stabilizers can also inhibit microbial growth [56].

Coagulation occurs by adding inorganic acids or acids/salts so that the stability of the NR and CNC colloid suspensions is disturbed. When a coagulant is added, the ionic strength of the aqueous medium changes so that the solid coagulates, the addition of the acid and / or an acid-cation combination neutralizes the anionic NR protective membrane covering membrane. The neutralized particles start colliding with each other. It also destroys the membrane allowing free movement of the polyisoprene polymer chains. This movement results in chain linkages and aggregations that trap the CNC nanoparticles. Ultimately this process forms the NR-CNC nanocomposite masterbatch. The change in ionic strength can reduce the thickness of the electric bilayer. This is what stabilizes the colloid and causes colloid aggregation through the Brownian movement [56].

IMPACT

Health Impact

Based on the results of a medical check-up at a rubber factory in 2018. Overall, workers an abnormality of 40%. The disorder consists of routine blood examination / BSS (4%), spirometry examination (17%), audiometry examination (35%), eye examination (eye vision) (18%) and eye examination (color blindness) (4%).

The results of the study found several diseases such as respiratory disorders, heart problems, and eye disorders. There are also skin disorders. The most common skin disorders are itching, redness and dry skin and scaly skin, while the body parts that suffer the most pain are the palms, arms, legs, neck, back and between the fingers [57].

Hazardous chemicals are at risk of causing liver dysfunction. Ammonia gas affects increased levels of Serum Glutamic Oxaloacetic Transaminase (SGOT) and Serum Glutamic Pyruvic Transaminase (SGPT) and decreases levels of malondialdehyde (MDA) [58], [59].

Environmental Impact

Based on reports from several rubber factories to the Palembang City Environment Agency about measurement results in liquid and air waste. NH_3 concentration in liquid waste at the inlet is 4.2 - 30.7 mg/L and at the outlet, there is 0.73 - 3.057 mg/L. Based on South Sumatra Governor Regulation No. 8 of 2012 for inlets, most are still above the quality standard and for the outlet, the results are below the quality standard. Measurement of NH_3 and H_2S gas concentrations from emissions and ambient air. NH_3 concentrations ranged from 0.0009 – 0.222 ppm and H_2S concentrations ranged from 0.0004 – 0.623 ppm. Based on Per.13 / Menaker / 2011; South Sumatra Governor Regulation Number 17 of 2005 and PP No. 41 of 1999 is still below the quality standard.

The coagulant, Sulfuric acid, TSP fertilizer, alum, and pineapple / pineapple juice, is acidic but does not have antibacterial and antioxidant properties to spur the development of natural antioxidant-destroying bacteria in the material. The growth of spoilage bacteria biodegrades protein in material to foul-smelling ammonia and sulfides, causing air pollution around it [60]–[63].

The results of measurements by Dahlan et al (2016) on rubber liquid waste with formic acid coagulant, liquid smoke, and sulfuric acid were listed in Table 3.

TABLE 3. Rubber wastewater with formic acid coagulants, liquid smoke and sulfuric acid

Parameter	Formic acid	Deurub K	Sulfuric acid
BOD (*Biological Oxygen Demand*)	198.8 mg/L	142.4 mg/L	102.8 mg/L
COD (*Chemical Oxygen Demand*)	497 mg/L	356 mg/L	497 mg/L
TSS (*Total suspended solid*)		336 NTU	

Source: [64].

With this value, the liquid rubber waste will pollute the environment if without prior processing.

CONCLUSION

Processing rubber material in South Sumatra, Indonesia, most farmers use coagulant are not recommended, namely sulfuric acid, alum, Triple Super Phosphate (TSP) fertilizer, a combination of sulfuric acid and alum, and others such as water of Dioscorea hispida, and water of tempe washing. These are acidic and cause the smelling of ammonia and sulfides. Wastwater of rubber material process can pollute the environment if it is not properly intervened. In a rubber factory, The process of managing rubber material can cause several illnesses for workers, but this is not known about its relationship with pollutants in the rubber factory environment yet.

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