RESEARCH ARTICLE



Environmentally safe preservation and stabilization of natural rubber latex in an acidic environment

¹SOAN Laboratorios, Bogotá, Colombia

²Polymer Engineering Center, Department of Mechanical Engineering, University of Wisconsin-Madison, Madison, Wisconsin, USA

Correspondence

T. A. Osswald, Polymer Engineering Center, Department of Mechanical Engineering, University of Wisconsin-Madison, Madison WI, 53711 USA. Email: tosswald@wisc.edu

J. C. Rodríguez Urbina¹ | T. A. Osswald²⁰ | J. E. Estela Garcia² | A. J. Román²⁰

Abstract

Natural rubber is an indispensable raw material that supplies about half of the world's rubber consumption. The latex that is extracted from the trees is composed of polyisoprene rubber, proteins, sugars, amino acids, lipids, and minerals. When the liquid latex emanates from the trees, it comes into contact with bacteria that cause it to decompose and coagulate. To hinder the decomposition and destabilization process, ammonia and other environmental and health hazard chemicals are added to the latex. The addition of these chemicals affects the health of plantation and rubber industry workers and results in residues that are contaminated with these chemicals, which require that processing facility effluents undergo costly treatment processes. Here, we present two novel liquid latex preservation and stabilization methods in an acid medium free of ammonia or other dangerous chemicals. The first method uses dodecyl benzene sulfonic acid to both stabilise and preserve the liquid latex, and the second uses ethoxylated tridecyl alcohol to stabilise and hydrofluoric acid to preserve the colloidal suspension. Both formulations result in rubber with superior mechanical properties, that is safe for the rubber plantation and industry workers, and with residues that no longer adversely affect the environment.

KEYWORDS

ammonia-free, latex, natural rubber, preservation, stabilization, viscoelasticity

INTRODUCTION 1

The rubber industry has experienced growth over time, reaching 30 million tons of rubber consumption per year in 2021, of which almost 14 million tons were natural rubber; this amounts to 2 kg of natural rubber per year for every person on the planet.^[1] Natural rubber is lauded for being a renewable resource and for being the most carbon-negative

biopolymer. A simplified chemical balance reveals that to produce a single kilogram of solid polyisoprene natural rubber, not including tree growth and the production of proteins, sugars, amino acids, and lipids present in the liquid latex, a Hevea brasiliensis tree roughly sequesters 3 kg of CO_2 and uses 1 kg of water, as it exudes 3 kg of oxygen.

This biological polymerisation plant that uses carbon dioxide as its primary raw material produces a fragile

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

^{© 2023} The Authors. SPE Polymers published by Wiley Periodicals LLC on behalf of Society of Plastics Engineers.

 TABLE 1
 Composition of Hevea brasiliensis tree liquid latex.

Component/Reference		RRIM ^[2]	Vaysse et al. ^[3]
Rubber		36	35
Proteins		1.4	1.5
Lipids	Neutral lipids	1.0	1.3
	Phospholipids	0.6	
Ash		0.5	
Carbohydrates		1.6	1.5
Nitrogen compounds		0.3	
Organic solutes			0.5
Inorganic substances			0.5
Water		58.5	59.7

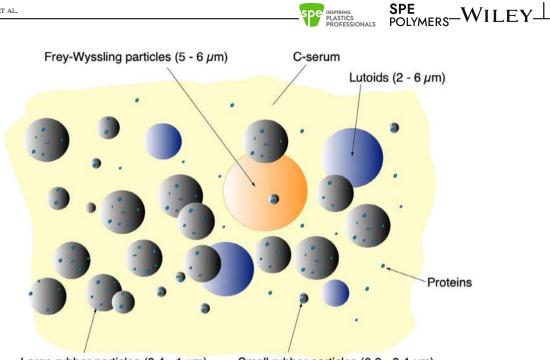
liquid latex, composed of approximately 35% by weight of rubber particles, 5% by weight of other solids, such as proteins, sugars, amino acids, lipids, and minerals, and 60% water^[2,3]</sup> (Table 1). The sugars, proteins, amino acids, and lipids render the liquid latex susceptible to rapid decomposition by bacteria and other living organisms when it comes into contact with air the moment it is extracted from the tree. The onset of putrefaction triggers an unwanted coagulation process, which renders the latex challenging to handle and process.^[4,5] Hence, the natural rubber producer is forced to use chemicals, such as ammonia, tetramethylthiuram disulfide (TMTD), and zinc oxide (ZnO) to stabilise and preserve the liquid natural rubber latex. Once these chemicals are added, the latex no longer decomposes, and it remains in a stable flowable condition.

However, ammonia, TMTD, and zinc oxide are harmful to the environment and the people handling the preserved and stabilised natural rubber liquid latex. The presence of these chemicals, in particular the strong smell of ammonia emanating from the liquid latex, does not go unnoticed in the field, processing plant, manufacturing facilities, and even in the final product. In the preface of his 2021 book, Empire of Rubber, Gregg Mitman writes that during a visit to the Firestone facilities in Liberia, the "smell of ammonia in the processing plant can be overpowering, as I learned when I too carelessly bent down to sniff the fast-moving latex flowing through the plant and was almost knocked unconscious".^[4] Mitman reported in his book that the handling of ammonia by the tappers was done without hand and eye protection. He went on to recount how ammonia "saturated the pores of a tapper's hands, deadened fingertips, and destroyed nails." He also recounted how some "went blind when the corrosive and caustic chemical got

into their eyes." Material safety data sheets classifies ammonia, or a mixture containing ammonia, as a corrosive material of *category 1B*, which leads to irreversible skin and eye damage.^[6] Material safety data sheets will also warn that ammonia causes severe skin burns, eye damage, and respiratory irritation. In addition, it also warns that ammonia is also an environmentally damaging substance of category 1, creating an acute hazard to aquatic environments. Similar to ammonia, TMTD is considered a harmful poisonous chemical that causes skin and eye irritation, which may cause an allergic skin reaction and damage to organs through prolonged or repeated exposure.^[7,8] It has also been documented that an elevated amount of TMTD can produce carcinogenic nitrosamines.^[9] Like ammonia, zinc oxide is also a category 1 environmentally damaging substance that creates an acute hazard to aquatic environments.^[5]

The stabilising effect of the chemicals inside the liquid latex that keep it from coagulating wanes over time, forcing the producer to process the latex into solid rubber or rubber products within a few months; at most, a stabilised latex has a shelf life of 6 months. The waste material that is left after extracting the solid rubber, which needs to be disposed of, contains ammonia, as well as sugars, proteins, amino acids, and lipids, which due to their contact with ammonia and TMTD, have been rendered useless. In his book, Mitman continues informing the reader that "for decades, the Firestone Plantations Company used the Farmington River as a convenient sink for dumping ammonia and other waste products generated in the industrial production of 'natural' rubber. Residents of nearby communities along the river who bathe, wash clothes, and fish in its waters had long complained of foul-smelling air, contaminated wells, skin rashes, and scarcity of fish. But not until 2008 was a wastewater treatment plant built, almost seventy years after the factory began processing latex." Such treatment plants include aerobic, anaerobic, and facultative ponds, which require large areas to expose wastewater to sunlight and oxygen.^[4–7,9]

Today, many countries recognise the need to regulate the amount of chemicals present in wastewater discharged from their processing plants. For example, in 2015, Colombia established stringent limits on chemical concentrations in effluents discharged by processing facilities such as the ones from the natural rubber industry.^[10] Some of these limits are hard to achieve, particularly for small growers and processing plants; 90% of rubber growers and processors are small-scale operations.^[11,12] The larger natural rubber-producing countries such as Thailand and Malaysia have similar



Large rubber particles $(0.4 - 1 \,\mu\text{m})$ Small rubber particles $(0.2 - 0.4 \,\mu\text{m})$

FIGURE 1 Liquid natural rubber latex. Latex is defined as a white colloidal cytoplasmic suspension composed of rubber particles, nonrubber particles, cytoplasmic C-serum, organelles, proteins, carbohydrates, and lipids.^[1,2] The rubber particles are composed of a lipid monolayer with a hydrophobic core made of *cis*-1,4-polyisoprene rubber molecules. Lutoids are acidic, osmosensitive, vacuole-like organelles that contain hydrolytic enzymes and proteins (B-serum) involved in various biological processes and are composed of a lipid bilayer surrounding a hydrophilic core comprised of B-serum.^[3] Lutoids are believed to sequester latex-agglutinating factors to avoid direct interaction with rubber particles, playing a large role in latex particle agglutination.^[4] C-serum is the metabolically active, aqueous phase of laticeferous cytoplasm, which contains about 60% of the latex proteins, including proteins that contribute to colloidal stability of the latex and rubber particles.^[9] Frey-Wyslling particles are non-rubber particles wrapped in a lipid bilayer with a yellow-orange colouring containing carotenoid pigments, oxidative enzymes, and other proteins.^[3]

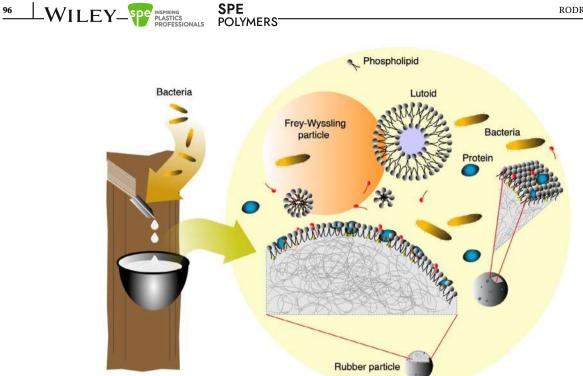
regulations, and large rubber treatment installations comply with the imposed standards. However, large amounts of pollution still exist because of discharges from smaller processors without treatment or because of inadequate maintenance of their treatment facilities.^[13] Even with these stringent regulations, the ammonia still present in the wastewater leads to high concentrations of nitrogen in effluents from rubber processing plants.^[14] This high concentration of nitrogen contributes to excessive nutrients in lakes and rivers, which promote dense unwanted algae growth, leading to the death of animal life, and in some places, such as southeast Asia, affecting their paddy fields. Furthermore, the high concentration of nitrogen has been attributed to methemoglobinemia, a blood disorder in infants.^[13]

This paper presents a novel preservation and stabilization technology for liquid latex that is environmentally friendly and free of ammonia, TMTD, ZnO, or other harmful chemicals.^[15] Due to the absence of ammonia, the novel method renders a natural rubber with a pleasant smell, which has a significantly reduced amount of volatile fatty acids (VFA) and has superior mechanical properties. Furthermore, after extracting the solid natural rubber, the residues no longer adversely affect the environment, and the sugars, amino acids, proteins, and lipids can be extracted and used for other applications. Finally, with the novel stabilisers and preservatives, the shelf life of liquid latex increases from a few months to a few years.

2 | LIQUID NATURAL RUBBER LATEX STABILISED WITH AN AMMONIA SOLUTION

When tapping the *Hevea brasiliensis* tree, an incision is made on the bark of the tree, severing laticiferous cells, which release a white and opaque liquid latex with a density between 0.97 and 0.98 g/cm³. The liquid latex is a colloidal dispersion of rubber particles, Frey-Wyssling particles, and lutoids inside a liquid cytoplasmic serum

95



Rubber tree

FIGURE 2 Rubber latex architecture before the putrefaction and coagulation process. The latex from an untapped Hevea tree is sterile, but after the first tapping, the latex vessels around the cut are contaminated by bacteria and other living microorganisms.^[1] Latex is susceptible to bacterial and enzymatic attacks, which leads to spontaneous coagulation, further promoted by the fragile lutoids, which contain agglutinating factors, like hevein. Volatile Fatty Acids (VFAs) are linear short-chain aliphatic mono-carboxylate compounds, generally malodorous, which are produced from sugar degradation by the metabolic activity of microorganisms, especially lactic acid bacteria. The proteins present in the serum play a large role in the evolution of rubber properties during maturation and coagulation.

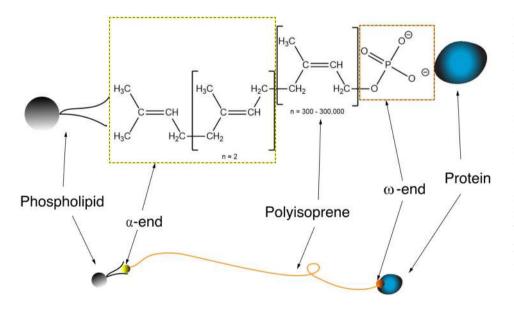


FIGURE 3 Possible polyisoprene molecular structure. It is commonly accepted that the chain elongation in the biosynthesis of natural rubber latex caps one end of the rubber molecule with either a mono- or diphosphate group, while the other end is capped with an isoprene-derived group.^[1] Currently, there is no structural evidence for the isoprene-derived group of Hevea natural rubber. However, there are reports indicating the association between the alpha-end and phospholipids,^[2] and the omega-end and proteins.^[3]

RODRÍGUEZ URBINA ET AL.

referred to as C-serum, composed of water, sugars, amino acids, proteins, lipids, and minerals, as schematically depicted in Figure 1.

The rubber particle size distribution is bimodal, with small particles ranging from diameters of 0.2 to 0.4 μ m, and large particles ranging from 0.4 and 2 μ m.^[16]

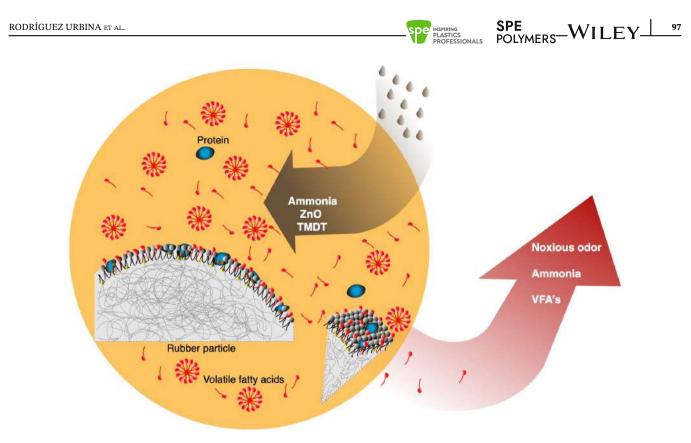
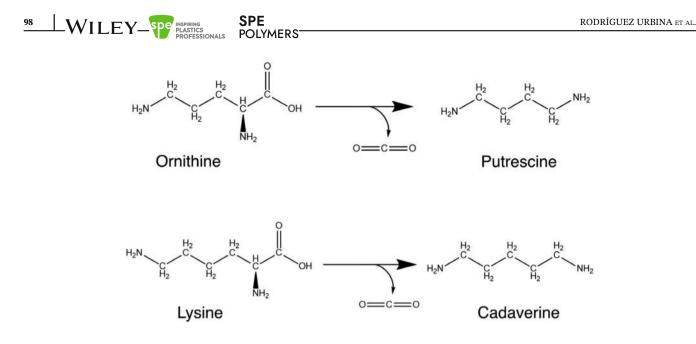


FIGURE 4 Ammonia stabilised rubber latex architecture. The addition of ammonia to natural rubber liquid latex is used as a preservative for longer-term storage.^[1] Ammonia acts as a bactericide and prevents the undesired reactions of the microorganisms to produce VFAs, while also hydrolyzing fatty acid esters to form soaps (salts of fatty acids) that act as stabilising bodies for the dispersed system. The yellow-orange colour is due to the release of colour-compounds from the Frey-Wyssling particles. Lutoids are easily broken down, but the release of B-serum in the ammoniated environment is unlikely to cause coagulation, as the preservative effect of ammonia is more prominent.

The rubber particles are encased in an approximately 20 nm thick layer of phospholipids and proteins that stabilise the rubber particle suspension within the serum. The phospholipids affix their hydrophobic tails on the rubber molecules inside a rubber particle's core, while pointing their hydrophilic heads toward the aqueous serum. Figure 2 is a schematic diagram of a rubber particle inside the serum. The rubber core is filled with polyisoprene chains, which, most researchers agree, have two end groups: an α -end and an ω -end. The α -end groups are mono- or diphosphate groups, attached through molecular interactions to the hydrophobic tails of the phospholipids (Figure 3). The ω -end groups are believed to be an isoprene-derived group, possibly another *cis*-1,4-isoprene, followed by two trans-1,4-isoprene molecules. These ω -end groups are attached to the proteins believed to be responsible for the biosynthesis of the polyisoprene chains inside the rubber particle.^[17] Although various plausible hypotheses exist of the structure of the end groups, no definite evidence is available to date of what they actually are.

As schematically depicted in Figure 2, lutoids are spherical particles that contain an aqueous solution filled

with sugars, amino acids, and proteins, often referred to as B-serum. The spherical aqueous core is surrounded by a bi-layer of phospholipids, with the hydrophilic heads of the inner laver pointing toward the B-serum, and the hydrophilic heads of the outer layer pointing toward the C-serum.^[18] The Frey-Wyssling particles are larger, fewer in number, and yellow in colour, due to the fact that they contain carotenoid, which give natural rubber its yellowish colour. The number of Frey-Wyssling particles and the amount of pigmentation can vary among different clones of Hevea brasiliensis trees.^[19]When fresh latex emerges from the wounded tree bark and starts running down the incision and into a container, it picks up bacteria, which attack the sugars, lipids, amino acids, and proteins, triggering a putrefaction process that simultaneously leads to coagulation.^[5] The bacteria feed on the sugars, lipids, and proteins, which are in charge of the stabilization of the colloidal dispersion of rubber particles.^[20] Furthermore, the bacteria attack the ornithine and lysine amino acids present in the liquid latex.^[21] which results in the formation of putrescine and cadaverine through decarboxylation, as given by



The formation of putrescine and cadaverine,^[22] in part, lead to the foul smell of the decomposing natural rubber latex.

The addition of an ammonia solution, resulting in a concentration between 0.35 and 0.8 wt% of ammonia in

the latex, stabilises the colloidal suspension by destroying the lutoids, and breaking down the phospholipids, resulting in a brown substance, believed to be magnesium ammonium phosphate, which darkens the final solid natural rubber.^[19,23] Furthermore, the ammonia degrades

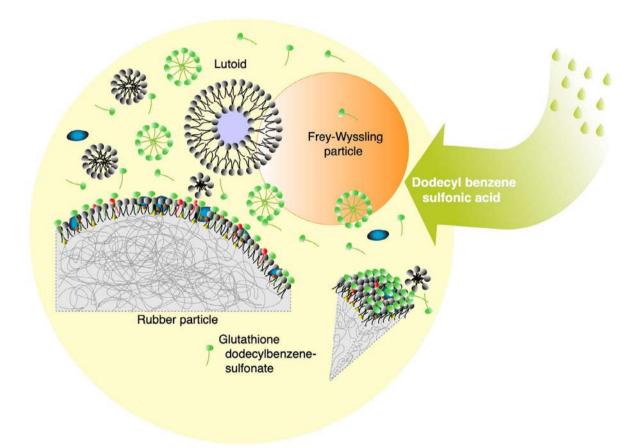


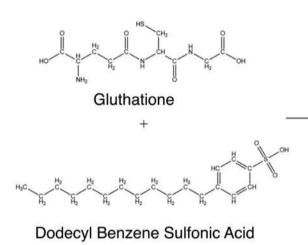
FIGURE 5 DBS stabilised and preserved rubber latex architecture. Glutathione-DBS (G-DBS) is believed to be involved in the reduction of bacterial activity and, due to its amphiphilic character, colloidal stabilization of the natural rubber latex.

the lipids, such as the phospholipids, forming additional volatile fatty acids, which aid in the stabilization of the rubber particles, as schematically depicted in Figure 4. The ammonia also breaks up the Frey-Wyssling particles, releasing the trapped carotenoid, which also contributes to the coloration of the final solid rubber.^[19] Large amounts of ammonia also help preserve the liquid latex by killing the bacteria; however, too much ammonia is not desired because of its adverse environmental health effects. Furthermore, the allowable concentration of ammonia in the final rubber material is classified in standards, such as ASTM D1076.^[24] Hence, other preservatives are used, such as TMTD, as mentioned earlier.



SPE _____WILEY _____

at least 4 years, with a pH of 3.5 and 4.2. This acidic environment is counterintuitive to anyone in the natural rubber tree latex industry, since liquid latex typically is maintained stable in alkalinic environments using ammonia, and is coagulated using acids, such as sulfuric or formic acid. Natural rubber liquid latex, stabilised with this technique, is being stored at 21°C at the University of Wisconsin-Madison where material is regularly tested and coagulated to ensure that stability and preservation throughout time has not been compromised. Future studies are required, but it is hypothesised that the DBS reacts with a tripeptide known as glutathione,^[25,26] composed of glutamate, cysteine and glycine, resulting in a molecule we refer to as glutathione dodecylbenzenesulfonate (GDBS) as shown below.

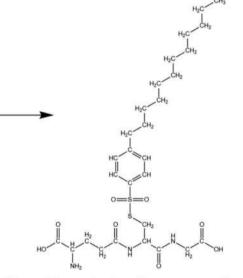


3 | AMMONIA-FREE STABILISED AND PRESERVED LIQUID NATURAL RUBBER LATEX

The new technology presented in this paper stabilises and preserves the liquid latex without the use of ammonia, TMTD or zinc oxide. Two methods are presented here, (1) treatment with a dodecyl benzene sulfonic acid (DBS) and (2) treatment with lauric alcohol (tridecyl alcohol) of several moles of ethylene oxide and hydrofluoric acid.

3.1 | Liquid latex stabilised and preserved with dodecyl benzene sulfonic acid

Within this work, it was proven that the treatment of natural latex with at least 2% by volume of dodecyl benzene sulfonic acid (DBS) leads to a preservation and stabilization of



Glutathione dodecylbenzenesulfunate

GDBS is hypothesised to serve two purposes: (1) as a surfactant that embeds its hydrophobic tail into the rubber particle, and directs its hydrophilic head toward the aqueous serum, as depicted in Figure 5, and, (2) as an antibiotic that kills the bacteria and preserves the liquid latex for an underminate period of time. We determined experimentally that 2 g of DBS are needed to preserve 100 g of natural latex. Below this proportion the latex coagulates, and above it is asymptotic in its behaviour. According to the stoichiometry of this reaction, 2 g of DBS produce 3.6 g of GDBS, necessary to preserve 100 g of liquid natural latex. Considering a purity of the acid of 96% we would have that 1.92 g of pure DBS produce 3.456 g of GDBS. With the continuous testing of the stabilised latex at the University of Wisconsin-Madison, we have shown that 2 g of DBS preserves and stabilises 100 g of natural rubber liquid latex for many years.

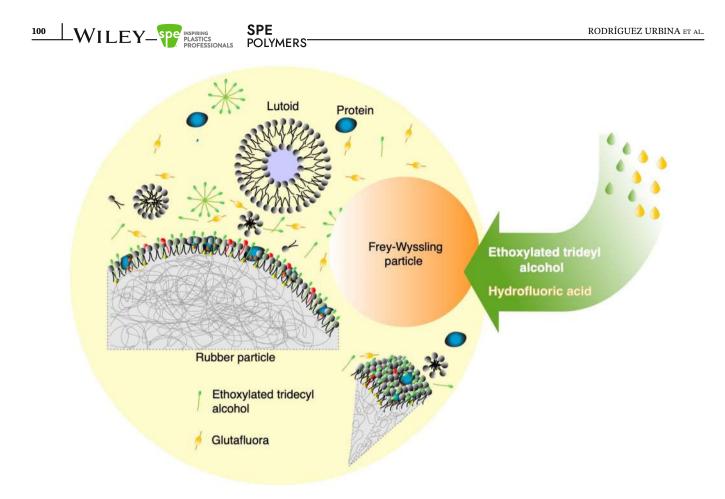
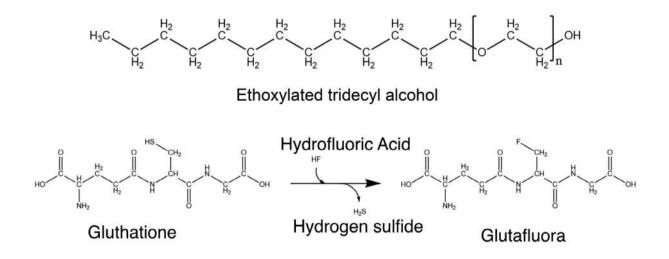


FIGURE 6 Ethoxylated tridecyl alcohol-stabilised and glutafluora-preserved rubber latex architecture. Ethoxylated tridecyl alcohol (ETA) is believed to stabilise the colloidal liquid latex suspension, including maintaining the presence of Frey-Wyssling particles and lutoids. The addition of hydrofluoric acid is believed to cause a reaction with glutathione, producing a compound with an apparent antibiotic effect referred to here as glutafluora. Thus, protecting the liquid latex against microbial activity.

3.2 | Liquid latex stabilised with ethoxylated tridecyl alcohol and preserved with hydrofluoric acid

Alternately, it was also demonstrated that adding 1% by volume of ethoxilated tridecyl alcohol, given by

stabilises the colloidal liquid latex suspension. Since the ethoxilated tridecyl alcohol still leaves the liquid latex susceptible to putrefaction, a 0.4% by volume of a 50/50 hydrofluoric acid/water solution was added to the liquid latex. It is hypothesised that the hydrofluoric acid reacts with the above-mentioned glutathione in the liquid latex,



forming a molecule, with possible antibiotic characteristics, which we call glutafluora, and given by

Glutafluora is believed to act as an antibiotic that prevents bacterial growth, which would lead to the decomposition of the natural rubber liquid latex. This reaction with the formation of hydrogen sulphide seems plausible, due to the fact that the liquid latex emanated a smell of decomposing eggs for a short time after the hydrofluoric acid was added to the latex. Figure 6 presents a schematic of the liquid latex stabilised with ethoxylated tridecyl alcohol and preserved with glutafluora.

4 | COAGULATION OF AMMONIA-FREE STABILISED AND PRESERVED NATURAL RUBBER LATEX

Test samples of the ammonia-free stabilised and preserved natural rubber latex have remained stable and pleasant smelling for a duration of at least 4 years at the University of Wisconsin-Madison. This is significantly longer than natural rubber latex stabilised with ammonia, where the latex is constantly undergoing a slow coagulation process, evident by a gradual increase in viscosity, resulting in a shelf life of at most 6 months.

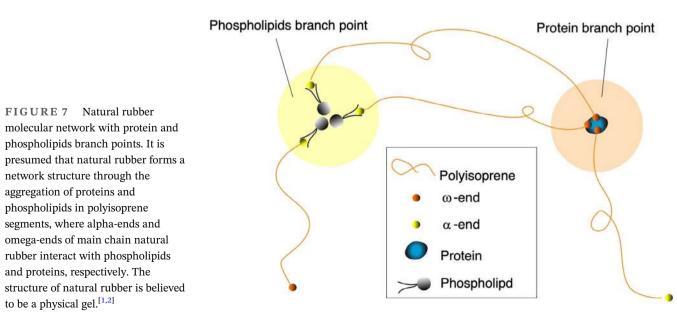
The coagulation process in stabilised natural rubber latex can be sped-up in the ammoniastabilised latex, or triggered in the ammonia-free latex, by the addition of substances that neutralise the negative charges on the outer surface of the rubber particles. Traditionally, environmentally unfriendly acids such as formic acid and sulfuric acids are used.^[27–29] Environmentally friendly substances such as alcohols were used in this study to coagulate the ammoniafree stabilised and preserved latex.



When a coagulating agent is added to stabilised latex, the negative charges on the rubber particles' skin are neutralised. Once this occurs, the surfaces of the rubber particles no longer repulse the surface of their neighbouring particles, allowing them to coalesce with one another, destabilising the colloidal dispersion of rubber particles. It is believed that as the negative charges on the surface of the particles are neutralised, the volatile fatty acid, phospholipid, and protein membrane that encases each rubber particle starts to break up and disperse throughout the serum. As a result of the coalescence, the polyisoprene molecules from different particles are allowed to intermingle with one another, creating a continuous solid rubber material. Many researchers hypothesise that the proteins believed to be responsible for the biosynthesis, and the phospholipids create branch points, which are responsible for the superior mechanical properties of natural rubber when compared to its svnthetic counterpart.^[30–32] Figure 7 presents a schematic of a polyisoprene molecular network with phospholipid and protein branch points.

Furthermore, because the stabilization process presented in this paper does not contain ammonia, the lysine, and ornithine, which remained untouched by the absence of ammonia, are believed to also act as chain extenders which can result in superior mechanical properties when comparing it to ammoniated natural rubber. This effect was confirmed by performing mechanical tests on ammonia-free and ammoniated natural rubber materials.

First, relaxation tests in tension were performed on rectangular strips of ammonia-free and ammoniated natural rubber using the Netzsch Gabo Eplexor 500N dynamic mechanical analyser (DMA). The 3 mm thick, 10 mm wide, and 20 mm long strips were subjected to a



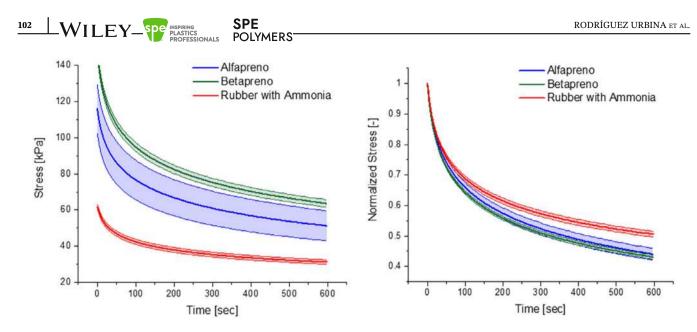


FIGURE 8 Results from the relaxation tests where the NETZSCH Gabo Eplexor 500N dynamic mechanical analyser was used to impose a 30% tensile strain on a rectangular specimen. The tests were conducted at 21°C and the strain was held for 10 min to comprehend the long-term viscoelastic behaviour of all three natural rubber samples; (1) the NR sample stabilised with DBS, (2) the ETA stabilised, and HF preserved NR, and (3) the ammoniated NR. The solid lines represent the average while the shaded region represents the standard deviation for each sample. As seen on the left, the novel NR stabilization and preservation techniques provide the user with a material with superior mechanical properties while ensuring that the relaxation behaviour does not vary significantly from an ammoniated NR sample, as seen on the right.

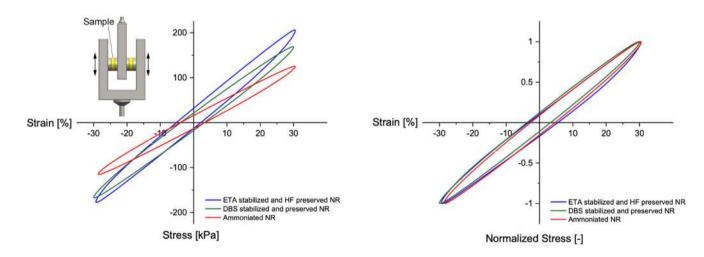


FIGURE 9 Results from the dynamic tests where the NETZSCH Gago Eplexor 500N dynamic mechanical analyser was employed to conduct cyclical testing of two cylindrical samples in double shear by imposing a 30% dynamic strain, at 1 Hz and at 21°C. Double shear ensured a pure shear loading condition, a feat uncapable of conventional single shear fixtures as the asymmetry in loading produces a bending moment. Testing was conducted on all three NR samples; (1) the NR sample stabilised with DBS, (2) the ETA stabilised, and HF preserved NR, and (3) the ammoniated NR. The experimental results seen on the left conclude that the novel stabilization and preservation techniques provide the user with a material with superior mechanical properties, all while resulting in similar tanδ values, represented by the similarity in elliptical Lissajous curves.

constant tensile strain of 30% while the DMA logged the stress response for 10 min. Figure 8 (left) presents the stress relaxation for the three different materials where it can be seen that a decrease in stress response is experienced by the sample over the 10-min test. The figure shows that the DBS stabilised and preserved rubber had an initial stress that was 2.5 times higher than the stress perceived by the ammoniated natural rubber. On average, the ETA stabilised, and hydrofluoric acid preserved natural rubber had an initial stress that was twice the stress felt by the ammoniated material. This is congruent with the hypothesis that the ammonia-free natural rubber has chain extenders that are not present in the natural rubber stabilised with ammonia. When the stress relaxation curves are normalised with respect to the initial stress for each test, as shown in Figure 8 (right), it is clear that ammonia-free materials have a slightly faster stress relaxation process. Shorter relaxation times are desirable when processing rubber as a prolonged relaxation time may render the material not processable without the use of plasticizers due to its highly viscoelastic nature.^[32,33]

The second test performed was a large amplitude oscillatory shear strain test, where two 1.5 mm thick, 10 mm diameter circular samples were subjected to a double shear sinusoidal strain with an amplitude of 30% and a frequency of 1 cycle per second, as schematically depicted in Figure 9 (left). A single shear loading scenario creates a moment load on the sample, which is not representative of a pure shear-driven load.^[34,35] For that reason, Netzsch's double shear fixture was implemented to ensure the moments were eliminated and a pure shear loading condition was reached. Figure 9 (left) presents the resulting Lissajous curves for the three materials considered. As expected, the stresses in ammonia-free natural rubber samples were higher than the stress in the ammoniated material; however, during the dynamic test, the ETA stabilised and hydrofluoric acid preserved natural rubber exhibited slightly higher stresses than the DBS stabilised and preserved rubber. In addition, it was interesting to see that when the Lissajous curves are normalised with respect to the maximum stress, as schematically depicted in Figure 9 (right), the shape of the curves is the same for all three materials. This means that the overall viscoelastic behaviour of the ammonia-free natural rubber is the same as the behaviour of the traditional ammoniated natural rubber.

5 | CONCLUSIONS

With the increased interest in sustainable materials, natural rubber research has resurfaced as a research topic around the world, from stabilization techniques,^[36] such as presented here, to life cycle analyses that show the how natural rubber products rise above any synthetic materials that it replaces.^[37] In this paper, we presented two novel liquid latex preservation and stabilization methods in an acid medium free of ammonia or other dangerous chemicals. We predict that this novel, counterintuitive method, of preservation of liquid natural rubber latex, in an acidic environment, will prove to be transformative in the natural rubber industry. The resulting materials have proven to produce rubber with superior



mechanical properties, that is safe for the rubber plantation and industry workers, and with residues that no longer adversely affect the environment, and that has a significantly longer shelf life than the existing alternatives.

CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

T. A. Osswald https://orcid.org/0000-0002-0243-0966 *A. J. Román* https://orcid.org/0000-0001-7077-6718

REFERENCES

- International Rubber Study Group. *Rubber Statistical Bulletin*. Vol 76, No. 7–9. International Rubber Study Group; 2021.
- 2. Rubber Research Institute of Malaysia. *Latex concentrate production and introduction to latex product manufacture.* Malaysian Rubber Board; 1992.
- 3. Vaysse L, Bonfils F, Sainte-Beuve J, Cartault M. Natural Rubber. In: Matyjaszewski K, Möller M, eds. *Chapter 10.8 in Polymer Science: A Comprehensive Reference.* Elsevier; 2012.
- 4. Mitman G. The Empire of Rubber Firestone's Scramble for Land and Power in Liberia. The New Press; 2021.
- Rojruthai P, Rodgerd P, Ho C-C, Sakdapipanich J. The use of 1,2-benzisothiazolin-3-one (BIT) in preparation of lowammonia and zinc-free natural rubber latex concentrate. *J Rubber Res.* 2021;24(5):783-795.
- Zinc Oxide, CAS-No 1314-13-2 [Online]; U.S. Zinc: Houston, TX, October 29 2012. http://hbchemical.com/wp-content/ uploads/2014/04/ZNO.pdf (Accessed April 4th, 2022)
- Ammonia, CAS-No 7664-41-7 [Online]; Sigma-Aldrich: St. Louis, MO, May 14 2020. https://www.sigmaaldrich.com/ US/en/sds/aldrich/294993 (Accessed April 4th, 2022)
- TMTD, Cas-No 137-26-8 [Online]; HB Chemical: Twinsburg, OH, June 18 2014. https://www.hbchemical.com/wp-content/ uploads/2014/04/TMTD-SDS.pdf (Accessed April 4th, 2022)
- 9. Crepy M-N. Rubber: new allergens and preventive measures. *Eur J Dermatol.* 2016;26(6):523-530.
- 10. Ministerio de Ambiente y Desarrollo Sostenible. Por la cual se establecen los parámetros y los valores límites máximos permisibles en los vertimientos puntuales a cuerpos de aguas superficiales y a los sistemas de alcantarillado público y se dictan otras disposiciones, Resolución 631 de 2015. 2015.
- 11. Bissonnette J-F, De Koninck R. Large plantations versus smallholdings in Southeast Asia: historical and contemporary trends land grabbing, conflict and agrarianenvironmental transformations: perspectives from East and Southeast Asia. *An Int Acad Conf.* 2015;12:5-6. Available: http://rcsd.soc.cmu.ac.th
- 12. Marimin MA, Darmawan M, Islam Fajar Putra MP, Wiguna B. Value chain analysis for green productivity improvement in

the natural rubber supply chain: a case study. *J Clean Prod.* 2014;85:201-211.

SPE

POLYMERS

- Mohammadi M, Man HC, Hassan MA, Yee PL. Treatment of wastewater from rubber industry in Malaysia. *Afr J Biotechnol*. 2010;9(38):6233-6243.
- Nguyen NH, Luong TT. Situation of wastewater treatment of natural rubber latex processing in the Southeastern region, Vietnam. J Viet Env. 2012;2(2):58-64.
- 15. Ammonia-Free Latex Compositions. US Patent Application 63/267,167. 2022.
- 16. D'Mello J. The handbook of microbial metabolism of amino acids. pp. 116–127. 2017.
- Tarachiwin L, Sakdapipanich JT, Tanaka Y. Relationship between particle size and molecular weight of rubber from Hevea Brasiliensis. *Rubber Chem Technol.* 2005;78(4): 694-704.
- Bottier C. Biochemical composition of Hevea brasiliensis latex: a focus on the protein, lipid, carbohydrate and mineral contents. *Adv Bot Res.* 2020;93:201-237.
- Sakdapipanich J. Deciphering the discoloration in the manufacturing of natural rubber. *IOP Conf Ser: Mater Sci Eng.* 2022;1234(1):012010.
- Salomez M, Subileau M, Intapun J, et al. Micro-organisms in latex and natural rubber coagula of Hevea brasiliensis and their impact on rubber composition, structure and properties. *J Appl Microbiol.* 2014;117(4):921-929. doi:10.1111/jam.12556
- Kumarn S, Churinthorn N, Nimpaiboon A, et al. Investigating the mechanistic and structural role of lipid hydrolysis in the stabilization of ammonia-preserved Hevea rubber latex. *Langmuir*. 2018;34(43):12730-12738. doi:10.1021/acs.langmuir. 8b02321
- Lichman BR. The scaffold-forming steps of plant alkaloid biosynthesis. *Nat Prod Rep.* 2021;38(1):103-129.
- 23. Santipanusopon S, Riyajan S-A. Effect of field natural rubber latex with different ammonia contents and storage period on physical properties of latex concentrate, stability of skim latex and dipped film. *Phys Procedia*. 2009;2(1):127-134.
- 24. ASTM D1076-15, Standard Specification for Rubber—Concentrated, Ammonia Preserved, Creamed, and Centrifuged Natural Latex. 2016.
- Nieto Rodrigues VM, Linares Prieto R. Avances Investigativos en Caucho Natural. Serie Tecnica. 1997;37:13-43. CONIF, Santafé de Bogotá.
- Jacob J, Seres JC. Development of Hevea latex diagnosis. Agritrop. 1988;12(2):97-115.
- Roy S, Namboodri CSS, Maiti BR, Gupta BR. Kinetic modeling of the epoxidation of natural rubber within-situ-formed peracid. SPE Polym Eng Sci. 1993;33(2):92-96.

- 28. Ehabe EE, Bonfils F, Sainte-Beuvre J, Collet A, Schué F. Hightemperature mastication of raw natural rubber: changes in macrostructure and mesostructure. *SPE Polym Eng Sci.* 2006; 46:222-227.
- 29. Kim C, Morel MH, Beuve JS, Guilbert S, Bonfils F. Better characterization of raw natural rubber by decreasing the rotor speed of Mooney viscometer: role of macromolecular structure. *SPE Polym Eng Sci.* 2010;50:240-248.
- Sriring M, Nimpaiboon A, Kumarn S, Sirisinha C, Sakdapipanich J, Toki S. Viscoelastic and mechanical properties of large- and small-particle natural rubber before and after vulcanization. *Polym Test.* 2018;70:127-134.
- Nun-anan P, Wisunthorn S, Pichaiyut S, Nathaworn CD, Nakason C. Influence of nonrubber components on properties of unvulcanized natural rubber. *Polym Adv Technol.* 2019; 31(1):44-59.
- 32. Rudolph NS, Osswald TA. Polymer Rheology: Fundamentals and Applications. Hanser Publishers; 2015.
- Osswald TA. Understanding polymer processing. Understanding Polymer Processing: Processes and Governing Equations. Carl Hanser Verlag; 2018.
- 34. Da Silva LF, Carbas RJC, Critchlow GW, Figueiredo MAV, Brown K. Effect of material, geometry, surface treatment and environment on the shear strength of single lap joints. *Int J Adhes Adhes*. 2009;29:621-632.
- 35. Cognard JY, Créac'Hcadec R, Maurice J. Numerical analysis of the stress distribution in single-lap shear tests under elastic assumption—Application to the optimisation of the mechanical behaviour. *Int J Adhes Adhes*. 2011;31:715-724.
- Promhuad K, Prasopdee T, Smitthipong W. Effect of natural extract from waste corn meal on stabilization of natural rubber. SPE Polym. 2021;2:172-178. doi:10.1002/pls2.10032
- Patrawoot S, Tran T, Arunchaiya M, Somsongkul V, Chisti Y, Hansupalak N. Environmental impacts of examination gloves made of natural rubber and nitrile rubber, identified by lifecycle assessment. SPE Polym. 2021;2:179-190. doi:10.1002/pls2. 10036

How to cite this article: Rodríguez Urbina JC, Osswald TA, Estela Garcia JE, Román AJ. Environmentally safe preservation and stabilization of natural rubber latex in an acidic environment. *SPE Polym*. 2023;4(3):93-104. doi:10. 1002/pls2.10089